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**FATE OF VOLATILE ORGANIC COMPOUNDS  
IN WASTEWATER COLLECTION SYSTEMS**

**Volumes IV - VIII**

**RAC Project No. 577G**

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# **Fate of Volatile Organic Compounds in Wastewater Collection Systems**

## **Volume IV: Biodegradation of VOCs in Sewers**

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M.Sc. thesis

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

September, 1994

## **5. BIODEGRADATION OF VOCs IN SEWERS**

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### **5.1 BACKGROUND**

As stated in Chapter 2, there is no published literature related to biodegradation of VOCs in sewers. As part of this study, extensive laboratory experiments were completed in order to obtain parameters which could be used to determine the significance of biodegradation relative to volatilization as a VOC fate mechanism in sewers. A brief overview of the research approach and major findings is provided here. The reader is referred to Volume IV of this report for a detailed description of methodologies and results.

### **5.2 EXPERIMENTAL METHODOLOGY**

The experimental methodology involved with this component of the overall research was tedious, consisting of numerous very complex steps. For the purposes of this discussion, only a brief summary of each of the major components is provided below. Detailed descriptions of experimental methodologies are provided as Volume IV of this report.

#### **Determination of Viable Biomass Levels in Municipal Sewers**

A rigorous review of existing literature indicated little information related to viable suspended biomass concentrations in sewers. Thus, on three separate days in 1993, wastewater samples were collected at four locations in the City of Guelph wastewater collection and treatment system. These locations included an industrialized sewer reach, a strictly residential sewer reach, the headworks (downstream of bar screens) at the Guelph Wastewater Treatment Plant, and an activated sludge reactor at the Guelph Wastewater Treatment Plant. A method based on adenosine triphosphate (ATP) analysis with the application of firefly enzymes and photoluminescence detection was employed to determine viable biomass concentrations at each of the sewer/headworks locations. Analyses of activated sludge were used as a reference (standard). Volume IV includes a detailed description of the ATP method.

## **Analysis of Sewer Biofilms**

A protocol was developed allowing for the growth of biofilms on stainless steel tags. Tags were submerged below the wastewater surface at the headworks of the Guelph Wastewater Treatment Plant. Individual tags were maintained in wastewater over a period of several weeks allowing for the growth of a viable biofilm. Tags were periodically retrieved from wastewater for one of two purposes: (1) analysis of biofilm characteristics, (2) use in laboratory reactors to assess VOC degradation by attached-growth microorganisms. Biofilm characteristics which were quantified included percent water content, average measured biofilm thickness, biofilm mass per unit area ( $\text{mg VSS}/\text{cm}^2$ ), and biofilm density ( $\text{mg VSS}/\text{cm}^3$ ). Detailed methodologies for determining these characteristics are provided in Volume IV.

## **Analysis of VOC Degradation**

Three sewer simulation reactors were designed and constructed entirely out of inert materials (glass, stainless steel, and teflon™). Reactor dimensions and features are described in detail in Volume IV. Each reactor was able to maintain a stainless-steel tag from the inside of its lid, allowing for complete submergence in the reactor liquid media (distilled, deionized water or untreated wastewater). Permeable Gortex™ tubing was used to supply oxygen to the water/wastewater in the reactor without allowing for bubbling and VOC stripping. Each reactor was spiked with either toluene, tetrachloroethene (perchloroethylene) or both. Contaminant concentrations were then monitored over a period of hours to days using a GC/FID or GC/ECD.

## **Determination of VOC Biodegradation Rate Constants**

Experimental data were analyzed using a statistical package to develop "lumped" (suspended and attached growth) biodegradation rate constants for each experiment.

## **Comparison of Biodegradation and Volatilization as Removal Mechanisms**

A spreadsheet program was developed in order to estimate the relative significance of biodegradation and volatilization as VOC fate mechanisms in

sewers. A hypothetical 5 kilometer sewer reach was used. Gas-liquid mass transfer coefficients were estimated based on the methods described in Chapter 4. Lumped biodegradation rate constants were based on the experiments described above.

### **5.3 RESULTS AND DISCUSSION**

#### **Viable Biomass Levels in Municipal Sewers**

The results of ATP analyses to determine suspended biomass concentrations in sewers are provided in Table 5.1. Additional characteristics of the wastewater at each sample location are also provided. At each location, dissolved oxygen concentrations were sufficient to maintain aerobic microorganisms. Concentrations of COD, VSS and TSS were consistent with many municipal sewer systems. Concentrations of VSS and TSS were typically lowest in the industrialized sewer reach.

Biomass concentrations ranged from a low of less than 0.01 mg/L in the industrialized reach to 23 mg/L at the plant headworks. In all cases, biomass concentration varied in the order of industrialized sewer, residential sewer, and plant headworks. This is not surprising as the industrialized sewer generally lacked a fecal source of microorganisms and the headworks effectively represents the cumulative (in both space and time) untreated wastewater in the sewer effluent (plant influent). Suspended microorganisms which were observed at the plant headworks had time to multiply during their transport within the collection system.

#### **Characteristics of Biofilms**

Over all experiments, the average water content of biofilms was only 72% (low relative to typical values of 95%+ for other attached-growth systems), with a standard deviation of only 3%. The average biofilm thickness was 290  $\mu\text{m}$ , with a standard deviation of 100  $\mu\text{m}$ . The average biofilm mass per unit area was 0.75 mg VSS/ $\text{cm}^2$ , with a standard deviation of 0.3 mg VSS/ $\text{cm}^2$ . The average biofilm density was 25 mg VSS/ $\text{cm}^3$ , with a standard deviation of 5 mg VSS/ $\text{cm}^3$ .

## Degradation Experiments

The results of "control" experiments are provided in Figures 5.1 and 5.2. In each case, either toluene or perchloroethylene was added to each of the three reactors, each of which was filled a priori with deionized water. Water samples were collected and analyzed over a 75 hour period. The control experiments suggest that little removal occurred in the reactors as a results of incidental gas release or sorption to reactor components.

Experiments were completed by adding toluene to all three reactors filled only with untreated (headworks) wastewater (no tag present) (Figure 5.3), and filled with untreated wastewater and a tag containing a biofilm (Figure 5.4). In both cases, toluene concentration decreased as a function of time. However, the data were not sufficient to ascertain the primary mechanism of removal, i.e., biodegradation by suspended versus attached microorganisms.

To study whether the microorganisms present in the experimental reactors were actually degrading toluene, i.e., as opposed to adsorption to biomass or suspended solids, two experiments were completed. In the first experiment, toluene was spiked into a reactor that contained untreated wastewater and a tag containing a biofilm. At approximately 80 hours after the initial spike, a second injection of toluene was completed. Results are presented in Figure 5.5. The reduction in toluene concentration following injection was similar to those illustrated in Figures 5.3 and 5.4. A second experiment was completed in a manner similar to that described above with one major exception. During the second toluene injection, a 0.1% yeast extract was also added to the reactor. Results are presented in Figure 5.6. Of significance is that the toluene concentration remained relatively constant following the second injection, suggesting that the microbes preferentially degraded the more easily degradable nutrients when they were made available. Had sorption, or another removal mechanism, been the primary mechanism for toluene removal, its effects should have been observed in Figure 5.6. They were not, suggesting that biodegradation was the primary removal mechanism for toluene during previous experiments.

Experiments similar to those described above for toluene were also completed for perchloroethylene. Results of five experiments involving

untreated wastewater, perchloroethylene and toluene addition, and no tag are presented in Figure 5.7. Unlike toluene, the perchloroethylene concentration was reduced only slightly (approximately 30%) over 75 to 90 hour periods. In part, this reduction may well have been due to adsorption to solids suspended in the wastewater. Three similar experiments were completed with single tags suspended in the wastewater during each experiment. Results are illustrated in Figure 5.8. Unlike the experiments involving only wastewater, addition of a tag led to a clear reduction in perchloroethylene concentration with time. These results suggest that perchloroethylene may be degraded by attached growth microorganisms, possibly within an anaerobic layer of the biofilm.

### **Experimental Biodegradation Rate Constants**

A commercial mathematical/statistical package was used to determine biodegradation rate constants for each experiment. Zero order, first order and Monod kinetic models were all tested. A first-order model was found to yield the best fit over all experiments. For each experiment, the effects of suspended and attached-growth biodegradation were "lumped" into an "effective" first-order biodegradation rate constant. Mass transfer effects, i.e., from wastewater to the biofilm interface, were not analyzed or considered.

Over all experiments, biodegradation rate constants were greater for toluene than for perchloroethylene. Rate constants for toluene ranged from  $7 \times 10^{-5}$  L/mg-VSS•hr to  $1 \times 10^{-4}$  L/mg-VSS•hr. Rate constants for perchloroethylene ranged from 2 to  $3 \times 10^{-5}$  L/mg-VSS•hr. A more detailed analysis of rate constants for each experimental variation is provided in Volume IV of this report.

### **Comparison of Biodegradation and Volatilization as Removal Mechanisms**

The spreadsheet model described previously was used in conjunction with gas-liquid mass transfer coefficients discussed in Chapter 4 and toluene biodegradation rate constants described above. A hypothetical 5 kilometer sewer reach was used. As listed in Table 5.2, a very conservative suspended biomass concentration of 100 mg-VSS/L was used, i.e., to overestimate biodegradation. Additional reach characteristics are described in Volume 4. Results of the simulation are also provided in Table 5.2. The toluene removal

efficiency for the 5 kilometer reach was predicted to be 65%. Despite the high suspended biomass concentration, 99% of the total removal was attributed to volatilization and eventual emissions to the ambient atmosphere. Model execution for other sewer configurations led to similar results, i.e., volatilization dominance over biodegradation as a toluene removal mechanism. With higher volatility and lower degradability, volatilization was also the dominant removal mechanism for perchloroethylene.

#### **5.4 SUMMARY AND CONCLUSIONS**

The major findings from this component of research were:

1. Toluene may be slowly biodegraded by both suspended and attached microorganisms in sewers.
2. Perchloroethylene may be slowly biodegraded by attached-growth microorganisms in sewers.
3. Volatilization is likely to dominate biodegradation as a VOC removal mechanism in most sewers.



Table 5.1 Suspended biomass concentrations in sewers

Date/Reach	Biomass mg MLVSS/L ± SD	pH	Temp °C	DO mg/L	CO <sub>2</sub> mg/L
February 11 industrial residential headworks	0.02 ± 0.0051 0.13 ± 0.11 19 ± 1.8	8.3 8.4 8.4	9.1 10.0 12.1	4.2 4.9 7.5	81-145 250-530 390-350
February 18 headworks	13 ± 3.4	8.5	12.1	7.8	290-650
March 2 industrial residential headworks	0.10 ± 0.05 0.14 ± 0.03 8.0 ± 3.7	6.4 8.8 8.1	11.5 12.1 10.3	6.4 6.2 6.2	710-800 530-580 450-520
March 9 industrial residential headworks	0.05 ± 0.01 0.50 ± 0.20 14.5 ± 3.4	6.6 6.8 7.6	11.1 13.7 12.5	5.4 8.4 8.5	450-460 540-690 140-240

DATE/REACH	TSS mg/L ± SD	VSS mg/L ± SD	ATP µg/ml ± SD	ATP content µg ATP/ g VSS
Feb 11/93 industrial residential headworks sludge	72 ± 8.4 110 ± 15 155 ± 37 2960 ± 110 n = 6	70 ± 10 113 ± 24 121 ± 19 2240 ± 105 n = 6	8x10 <sup>-6</sup> ± 1.8x10 <sup>-6</sup> 5x10 <sup>-3</sup> ± 3.7x10 <sup>-3</sup> 0.007 ± 0.0016 0.9 ± 0.005 n = 3	0.11 0.44 58 400
Feb 18/93 headworks sludge	176 ± 46 2740 ± 32 n = 6	146 ± 37 2120 ± 258 n = 6	0.02 ± 0.006 3.5 ± 0.022 n = 3	140 240
March 2/93 industrial residential headworks sludge	208 ± 23 106 ± 11 220 ± 100 2240 ± 350 n = 6	183 ± 21 94 ± 5 188 ± 67 1700 ± 249 n = 6	8x10 <sup>-5</sup> ± 4.1x10 <sup>-5</sup> 1x10 <sup>-4</sup> ± 2.0x10 <sup>-5</sup> 0.006 ± 0.003 1.3 ± 0.003 n = 3	0.44 1.1 32 760
March 9/93 industrial residential headworks sludge	78 ± 27 136 ± 39 238 ± 67 3420 ± 117 n = 6	67 ± 21 108 ± 36 198 ± 65 2810 ± 136 n = 6	3x10 <sup>-4</sup> ± 6.5x10 <sup>-4</sup> 3x10 <sup>-5</sup> ± 0.0001 0.009 ± 0.002 1.4 ± 0.004 n = 3	4.5 0.27 45.5 500

Table 5.2 Parameters and results of biodegradation/volatilization modeling

Contaminant Characteristics		Sewer Characteristics	
Toluene		Diameter(m)	0.5
$H_c \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$	0.23	Slope (m/m)	0.005
$K_{\text{bio}}$ ( $\text{m}^3/\text{gMLVSS}\cdot\text{s}$ )	$4.6 \times 10^{-4}$	Roughness	0.014
Initial concentration ( $\text{mg}/\text{m}^3$ )	100	Length of pipe (m)	5000
		Temperature (K)	293

	Case 1	Case 2	Case 3
Vent rate ( $\text{m}^3/\text{s}$ )	0.11	0.11	0.11
$X_a$ ( $\text{g MLVSS}/\text{m}^3$ )	0.1	1	20
$K_{\text{ra}}$ (1/hr)	0.74	0.74	0.74
Depth (m)	0.15	0.15	0.15
Removal %	66	69	97
% stripped	99	90	32
% biodegraded	1	10	68

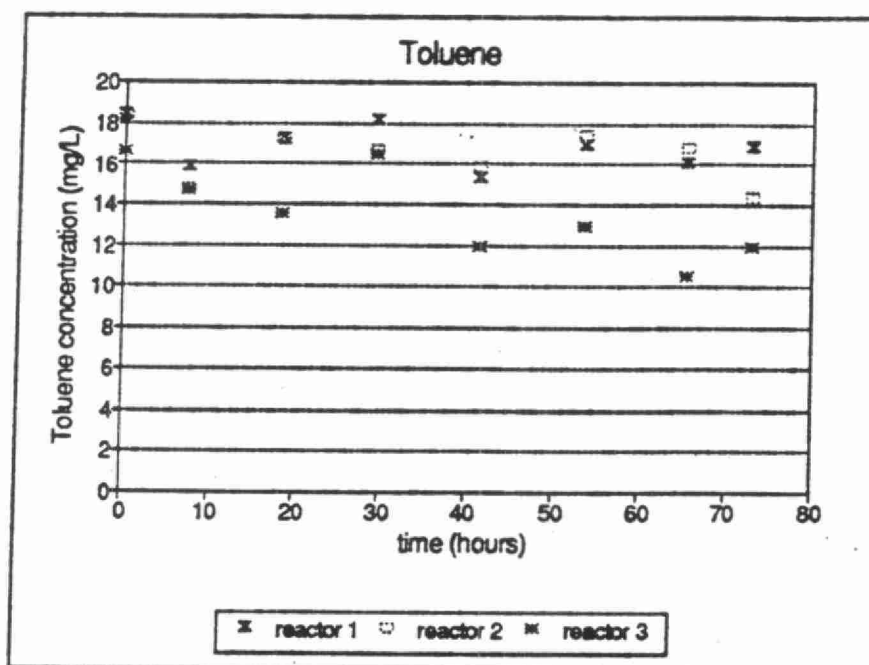


Figure 5.1 Toluene concentration versus time for sterile control experiment

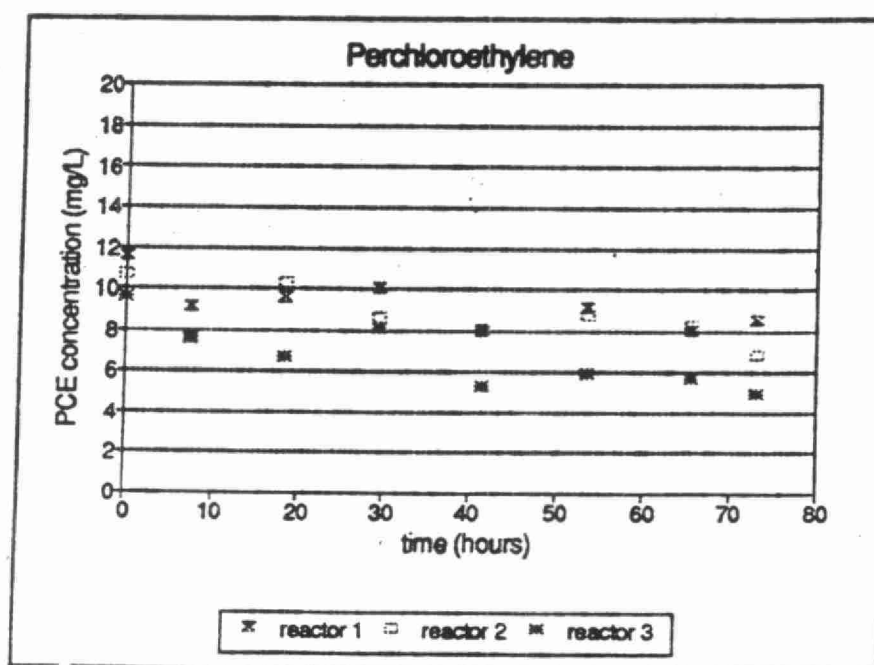


Figure 5.2 Perchloroethylene concentration versus time for sterile control experiment.

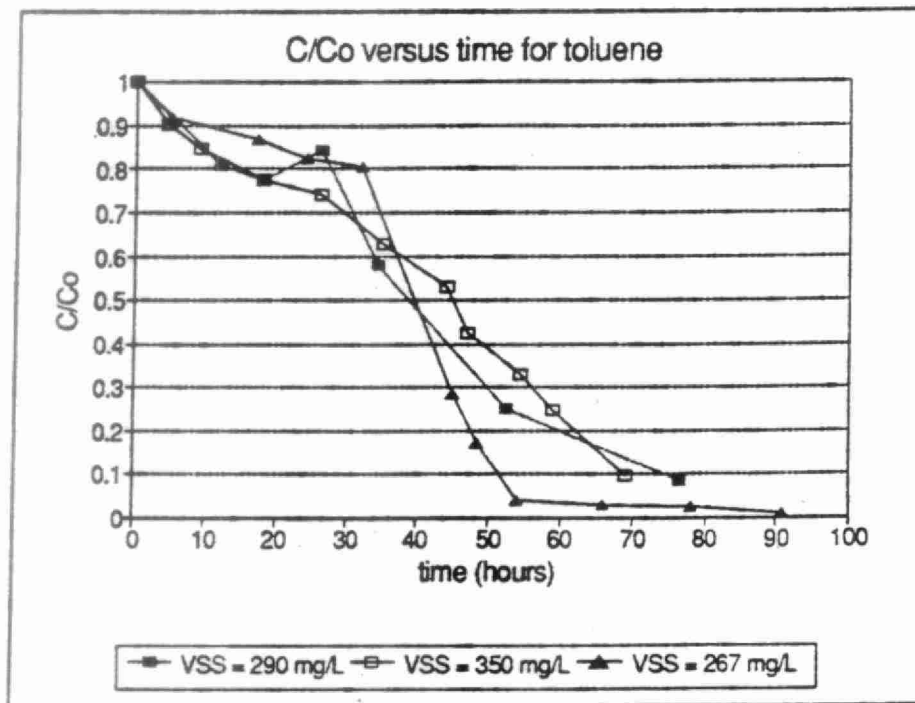


Figure 5.3 Toluene concentration versus time (wastewater only)

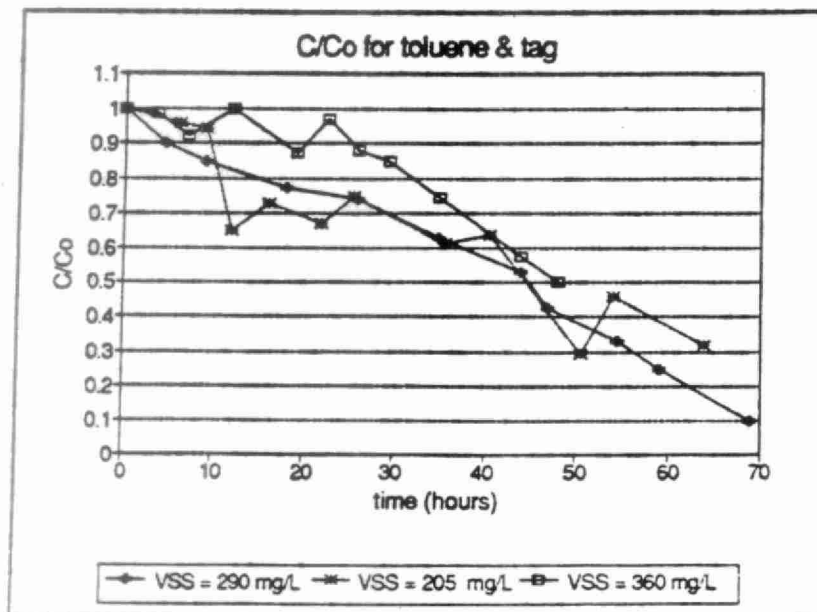


Figure 5.4 Toluene concentration versus time (wastewater and tag).

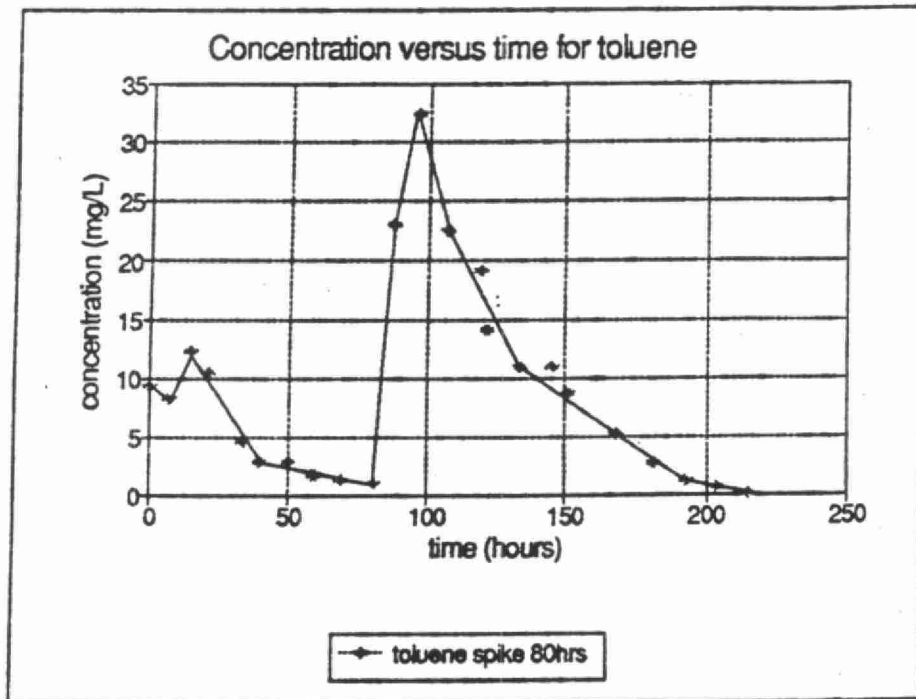


Figure 5.5 Toluene concentration with intermediate injection (wastewater and tag)

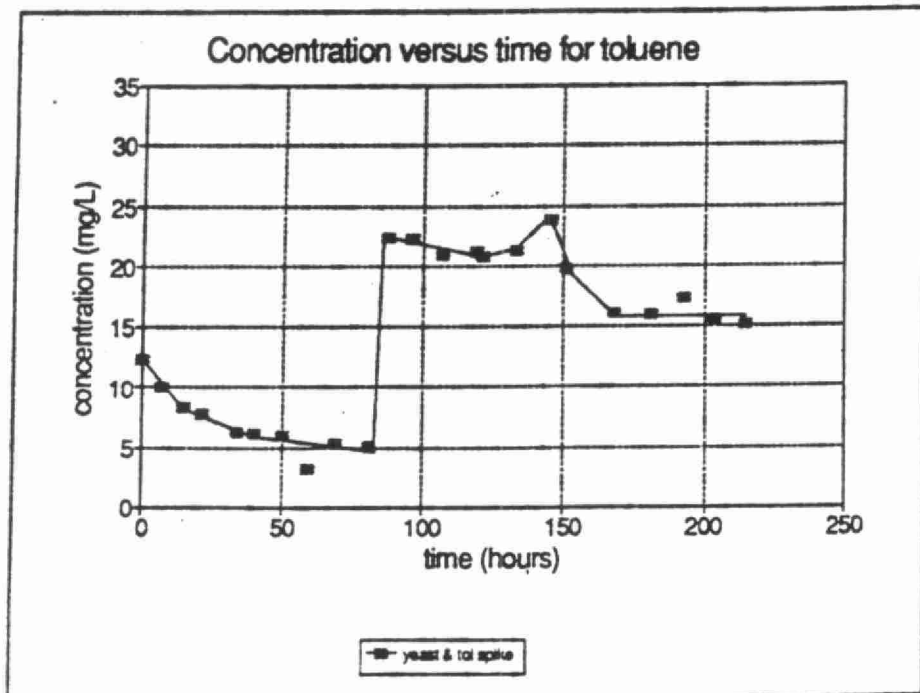


Figure 5.6 Toluene concentration with intermediate injection (wastewater, tag and yeast)

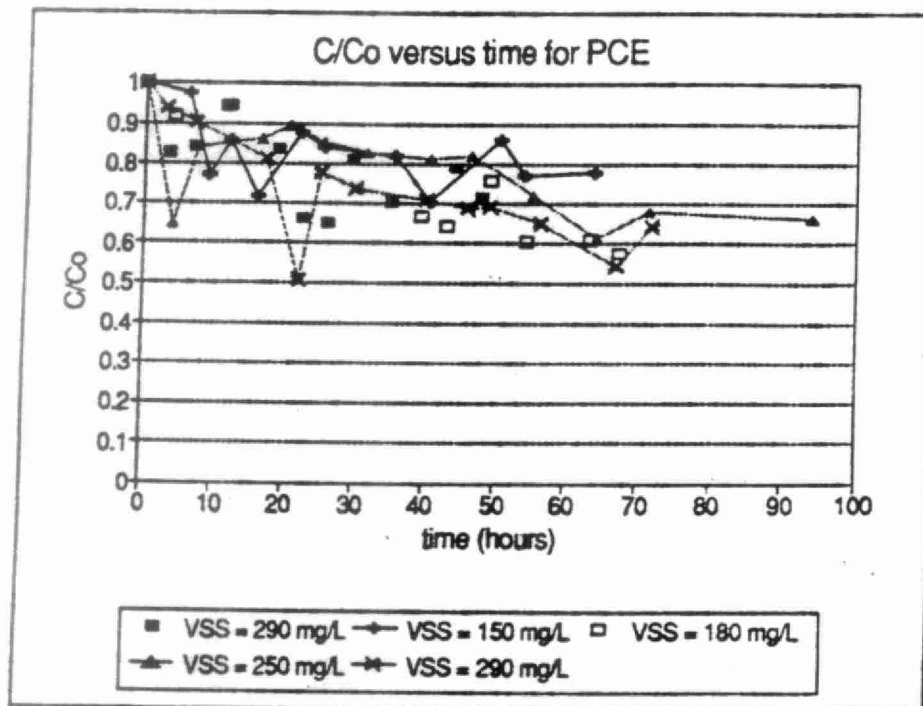


Figure 5.7 Perchloroethylene concentration versus time (wastewater, PERC and toluene only)

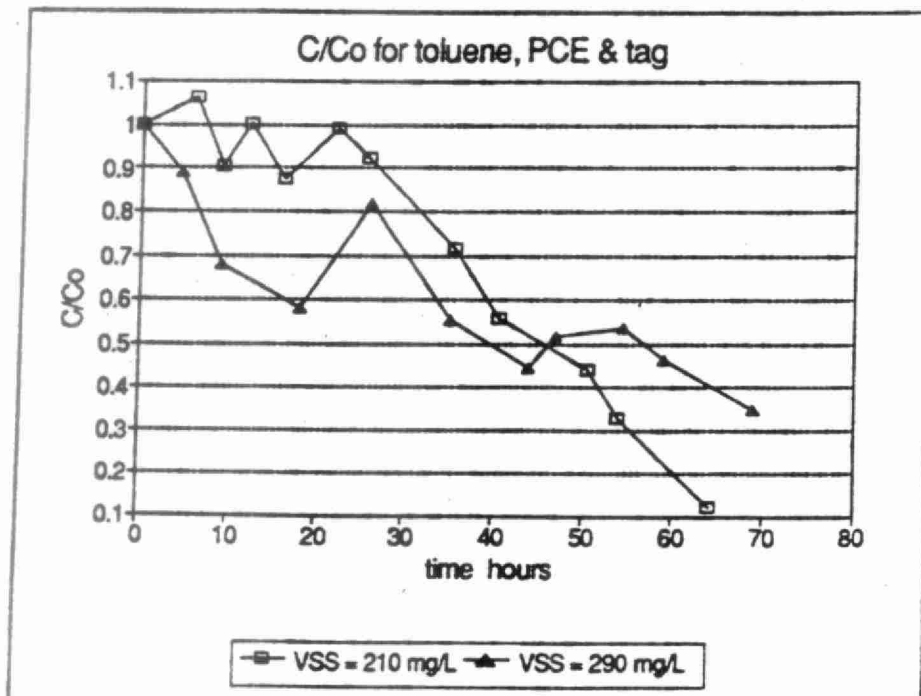


Figure 5.8 Perchloroethylene concentration versus time (wastewater, tag, PERC and toluene)

# BIODEGRADATION OF VOLATILE ORGANIC COMPOUNDS IN SEWERS

A Thesis

Presented to

The Faculty of Graduate Studies

of

The University of Guelph

by

MICHEL SWANSTON

In partial fulfilment of requirements

for the degree of

Master of Science

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## ABSTRACT

### BIODEGRADATION OF VOLATILE ORGANIC COMPOUNDS IN SEWERS

Michel Swanston  
University of Guelph, 1994

Advisor:  
Dr. R. Corsi

The biodegradation of volatile organic compounds (VOCs) was the focus of the research presented in this thesis. The research involved sampling wastewater in municipal sewers to estimate viable biomass concentrations and the construction of lab-scale reactors to test biodegradation of VOCs.

Adenosine triphosphate analysis was used to estimate viable biomass quantities in raw wastewater taken from residential sewer lines, industrial sewer lines and the headworks of a wastewater treatment plant. The proportion of volatile suspended solids in sewers that is viable biomass was found to be very small.

In the reactors, wastewater and slime layers biodegraded the two test VOCs, toluene and tetrachloroethylene. Biodegradation rate constants for these two chemicals were determined and used in a simple two-phase steady-state computational model to compare, biodegradation and stripping of VOCs along a uniform steady-state sewer reach. Stripping of the VOCs was the dominant removal mechanism predicted by the model.



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## ABBREVIATIONS

The following abbreviations are used in this thesis:

ATP	Adenosine triphosphate
COD	Chemical oxygen demand
DO	Dissolved oxygen
EDTA	Ethylenediamine tetra-acetic acid
FID	Flame ionization detector
GC	Gas chromatograph
GWTP	Guelph wastewater treatment plant
HSS	Head space sampler
IAWQ	International Association on Water Pollution Research and Control
MCI	Massey Creek interceptor
MISA	Municipal/Industrial Strategy for Abatement
MLVSS	Mixed liquor volatile suspended solids
MW	Molecular weight
NESHAP	National Emission Standards for Hazardous Air Pollutants
OUR	Oxygen Uptake Rate
PCE	Tetrachloroethylene
S	Solubility
TSS	Total suspended solids
VOC	Volatile organic compound
VP	Vapour pressure
VSS	Volatile suspended solids
WCS	Wastewater collection systems
WWTP	Wastewater treatment plant



## INTRODUCTION

---

Volatile organic compounds (VOCs) are chemicals that easily volatilize from water to air. They are discharged to municipal wastewater collection systems (WCS) from a variety of sources such as, industry, commercial facilities and private residences. Many VOCs found in wastewater are believed to be toxic. Benzene, tetrachloroethylene and dichloromethane are VOCs typically found in sewers, and they are known or suspected carcinogens. The release of these chemicals into sewers raises two major concerns. The chronic health risks to workers at wastewater treatment plants and the general public are the most important. Many VOCs are also classified as reactive organic gases that can contribute to the production of ozone in urban airsheds. (Corsi *et al.*, 1992).

Concerns over the release of air pollutants into the atmosphere have resulted in regulations for their control. In the United States, National Emission Standards for Hazardous Air Pollutants (NESHAP) were drafted as a result of the Clean Air Act of 1990. The Municipal-Industrial Strategy for Abatement (MISA) program has been developing regulations for the control of toxic chemicals discharged into any water resources in Ontario, including sewers. MISA has developed a sewer use control program under which municipalities will be required to undertake new responsibilities for monitoring and regulating discharges to municipal sewer systems. The Ontario Ministry of the Environment and Energy (MOEE) will eventually promulgate a municipal sewer use by-law to enforce effluent limits and other controls. This research will aid in the development of the proposed sewer use by-laws (MOEE, 1988).

The mass loading of VOCs received at wastewater treatment plants is an unknown fraction of total VOCs discharged to sewers. However, there has been little work completed to determine the fate of VOCs in sewers. Most of the work has focused on volatilization as the primary removal mechanism of VOCs, while biodegradation has not been investigated. Biological activity is known to occur in sewers, and it is conceivable that aerobic and / or anaerobic biodegradation of VOCs can occur in wastewater by suspended biomass. The slime layer attached to wetted sewer walls is also a potential site for biodegradation of VOCs. The research described in this thesis was undertaken to investigate the potential biodegradability of VOCs by suspended biomass and slime layers attached to wetted sewer walls.

## **1.1 OBJECTIVES**

The overall objective of this thesis was to assess the potential for biodegradation of VOCs in municipal sewers. Specific research objectives included:

- (1). Determination of suspended biomass concentrations in residential and industrial sewers and raw composite wastewater, i.e. from the headworks of a wastewater treatment plant.
- (2). Use of the information obtained in objective (1) to determine the importance of biodegradation of VOCs by suspended biomass relative to volatilization along a uniform sewer reach.

- (3). Development of laboratory reactors that simulate biofilms growing along wetted sewer walls.
- (4). Use laboratory reactors to determine the extent to which toluene and tetrachloroethylene can be biodegraded by biofilms and suspended biomass in wastewater in sewers.
- (5). Determination of whether biodegradation of VOCs by biofilms is significant relative to volatilization.

## **1.2 SCOPE OF WORK**

To accomplish the first objective, four sampling events at two municipal sewer lines and the Guelph wastewater treatment plant (GWWTP) were carried out. Adenosine triphosphate (ATP) analysis was used to estimate biomass concentrations in residential, industrial and raw-composite wastewater and activated sludge.

To study the activity of the slime layer, three laboratory scale reactors were constructed and experiments using toluene and tetrachloroethylene (PCE) as sample VOCs were completed. Stainless-steel tags were suspended in the headworks of the Guelph wastewater treatment plant. The slime layers that grew on these tags were tested in these reactors to determine whether biodegradation of the two target VOCs was possible.

A simple two-phase, steady-state model was developed to determine the significance of biodegradation of these two VOCs compared to volatilization.

### 1.3 ORGANIZATION

Background information on biodegradation of VOCs, viable biomass concentrations in sewers and biofilm biodegradation is provided in chapter 2. Chapter 3 contains a description of the model used to compare volatilization and biodegradation. The methodology for the determination of active biomass in sewers is described in chapter 4, with the results of the four sampling events presented in chapter 5. The model analysis using the calculated viable biomass concentrations is presented in chapter 6. Chapter 7 details the methodology used in the reactor experiments, the results of which are presented in chapter 8. The determination of a biodegradation constant and its use to predict toluene removal along a sewer reach is presented in chapter 9. Conclusions, recommendations for future research and references are presented in chapters 10, 11 and 12 respectively.

## BACKGROUND

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There are four primary mechanisms that may affect the fate of VOCs in sewers. These are volatilization, sorption to solid particles, biodegradation by microbes and generation / removal by chemical reactions in the wastewater. These mechanisms occur simultaneously, making the fate of VOCs in sewers a very complex issue. Volatilization has been regarded as the primary mechanism for the removal of VOCs from sewers (Corsi *et al.*, 1993), however, there have been no reported studies related to the biodegradation of VOCs in sewers.

### 2.1 SUSPENDED BIOMASS IN SEWERS

Microorganisms suspended in raw wastewater include bacteria, protozoans, fungi and algae. These organisms are for the most part facultative anaerobes (i.e. able to live under aerobic or anaerobic conditions). The largest concentration of bacteria typically found in untreated domestic wastewater include fecal coliforms, fecal streptococci and enterococci. Other types of bacteria may include *Salmonella sp.*, *Pseudomonas sp.*, *Clostridium sp.* and *Bacillus sp.*. Helminth ova, protozoan cysts, cryptosporidium cysts and enteric viri are other organisms that can also be found in domestic wastewater (Metcalf and Eddy, 1991). The types of waste and operating conditions will influence the types of microbes that eventually colonise activated sludge reactors in a wastewater treatment plant (WWTP).

The concentration of suspended biomass will probably vary from one sewer to another, depending on the environmental conditions in each sewer. This parameter is an important indicator of the likelihood of biodegradation by suspended biomass. Presently, there is little published information on the concentration of biomass in sewers. Jorgenson *et al.*, (1992) estimated that the amount of viable biomass in wastewater ranged from 8-30% of the suspended solids in wastewater. This was based on adenosine triphosphate analysis (ATP), oxygen uptake rates (OUR) and fluorescein diacetate measurements. They also found that ATP and OUR analyses provided reliable methods for the determination of viable biomass in wastewater and activated sludge. Henze (1986), after a literature review, suggested a maximum OUR of  $150 \text{ mg O}_2/(\text{g VSS h})$  for bacteria in the exponential growth phase. Using this value, he estimated that viable biomass can make up 6-78% of VSS depending on the type and treatment of the wastewater.

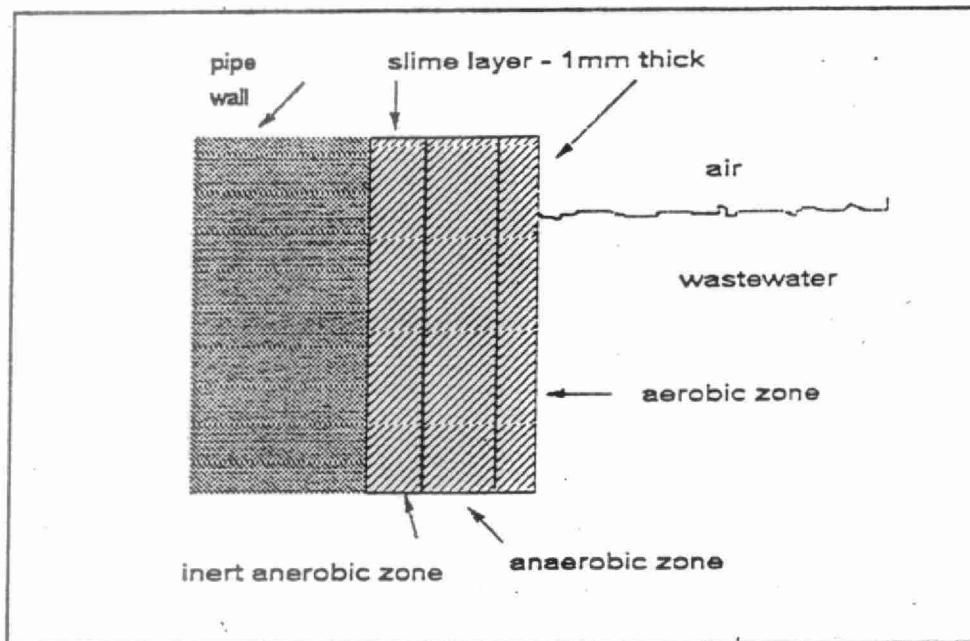
Sollfrank and Gujer (1990) determined the fraction of heterotrophic biomass in the primary effluent wastewater in the City of Zurich to be 70 mg COD/L. This fraction of heterotrophic biomass was a parameter in a biokinetic model suggested in 1986 by the (International Association on Water Pollution Research and Control) IWAPRC Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment (Henze *et al.*, 1987). The model required the authors to differentiate the organic matter in wastewater into five fractions, (inert, soluble and particulate, readily and slowly biodegradable, heterotrophic biomass). This biokinetic model allows the prediction of organic matter degradation, nitrification and denitrification in a single-sludge activated sludge systems.

Kappeler and Gujer (1992) determined the heterotrophic biomass of wastewater and activated sludge using a batch reactor with neither substrate nor oxygen limitations. They developed an equation based on process kinetics and the OUR in the batch reactor that they used to estimate the concentration of heterotrophic biomass in wastewater. They reported a viable heterotrophic biomass of 18 mg COD/L for primary effluent (domestic and industrial in origin) for the Flawil WWTP. A value of 65 mg COD/L of heterotrophic biomass was determined from settled domestic wastewater at Teffenwies WWTP, Zurich. At Dietikon WWTP the viable heterotrophic biomass was determined as 49 mg COD/L. A value of 0.45 mg VSS /mg COD can be used as the yield coefficient for heterotrophic biomass found principally in domestic wastewater (Ekama *et al.*, 1986). Using this value, 18 mg COD/L, 65 mg COD/L and 49 mg COD/ L are equivalent to 8 mg VSS /L, 29 mg VSS/L and 22 mg VSS/L respectively of heterotrophic biomass.

Lokkegaard *et al.*, (1994) used an equation similar to that developed by Kappeler and Gujer (1992) to estimate the concentration of viable heterotrophic biomass in the Emscher river, Germany to be approximately 16 mg/L. The Emscher river was acting as a large wastewater collector receiving untreated and mechanically treated wastewater. The above information suggest that the quantity of biomass in the sewer can vary significantly.

## 2.2 BIOFILMS

The slime layer attached to a wetted sewer wall is called a biofilm. It is an attached microbial population existing within a matrix of extracellular polymeric substances created by the organisms (Blenkinsopp and Costerton, 1989). An illustration of a sewer biofilm is provided in Figure 2.1.



**Figure 2.1.** A cross section of a biofilm layer in a pipe showing the various active zones. Adapted from (USEPA, 1985).

Depending on the wastewater velocity, abrasive content and other environmental conditions, the thickness of the biofilm can range from 0.3-1.0 mm (USEPA, 1985). Base biofilm consists of an organized accumulation of bacteria and extracellular polymeric substances which have a clearly defined boundary (Characklis and Marshall, 1992).



The availability of oxygen determines the relative thickness of the aerobic and anaerobic zones. In thick biofilms the base region is generally anaerobic, because diffusion is the dominant transport mechanism and an oxygen gradient develops as the surface layer of the film consumes the oxygen first (USEPA, 1985). Chemical microgradients and pH gradients can develop within biofilms as heterogeneity increases within the biofilm. Biofilm bacteria are inherently less sensitive than suspended bacteria to drying, surfactants and biocides (Blenkinsopp and Costerton, 1989).

Biofilms are found in many natural aquatic systems, especially those with a high surface area and low nutrient content. They can be found in streams, cooling towers, water pipes and on animals. They have been utilized in wastewater treatment in trickling filters and rotating biological contactors, where the biofilms can remove the carbonaceous biological oxygen demand (BOD) and nitrogen to acceptable levels (Patty and Chapman, 1989).

The processes for which biofilms have been used in wastewater treatment such as nitrification and denitrification in rotating biological contactors are relatively well understood and modelled. Neilson *et al.*, (1992) concluded that existing biofilm models based on lab studies may not predict microbial changes in sewers very well. Sewer biofilms are not well understood, they experience high organic loading rates and high shear stresses because of high flow velocities of wastewater. As a result, the multi-species surface of the biofilm in the sewer is sloughed off and tends to be rough. This rough biofilm-bulk liquid interface can have a significant effect on mass transfer processes.

## 2.3 VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds are chemicals that have high Henry's law coefficients i.e. greater than  $10^{-3}$  atm m<sup>3</sup>/mol or 0.1 [m<sup>3</sup><sub>liq</sub>/m<sup>3</sup><sub>gas</sub>]. They tend to have low solubilities in water, boiling points less than 100°C and vapour pressures greater than 1 mm Hg at 25 °C (Metcalf and Eddy, 1991). These compounds are used as both industrial and commercial solvents, however they are also found in household products such as paint removers and cleaners. Thus, VOCs have been observed in municipal (Reid and McEnvoy, 1987) as well as industrial sewers.

The two VOCs that will be addressed in this study are toluene and tetrachloroethylene. They are two of several targeted VOCs that were studied in the project, Fate of Volatile Organic Compounds in Wastewater Collection Systems, funded by Ontario Ministry of Environment and Energy. Toluene is generally considered to be easily biodegraded aerobically. In activated sludge systems it is a VOC that is biodegraded rather than stripped (Blackburn *et al.*, 1985; Namkung and Rittman, 1987; Parker *et al.*, 1993). This is in contrast to tetrachloroethylene, which tends to have zero to very low biodegradation rates in aerobic systems (Bouwer *et al.*, 1985; Kobayshai *et al.*, 1982; Ram *et al.*, 1990).

### 2.3.1 Toluene & Tetrachloroethylene (PCE)

Toluene is a monocyclic aromatic compound with one methyl group. It is moderately soluble in water and tends to partition into the gas phase. It is used as a solvent in paints and varnishes, in pesticides, as a cleaning agent and in chemical extractions (CEPA, 1992). Tetrachloroethylene is a non-flammable liquid that is relatively insoluble in water. It is the principal solvent used in the dry-cleaning industry and is present in household products such as suede protectors and paint removers and strippers (CEPA, 1993).

**Table 2.1 Some properties of Toluene and Tetrachloroethylene (PCE)**

Compound	M.W.* g/mol	Henry's Law* constant atm m <sup>3</sup> /mole at 20°C	S* mg/L at 20°C	V.P.* mm Hg at 20°C
Toluene	92.1	0.00555	515	22
PCE	165.8	0.0141	140	18

M.W. = molecular weight

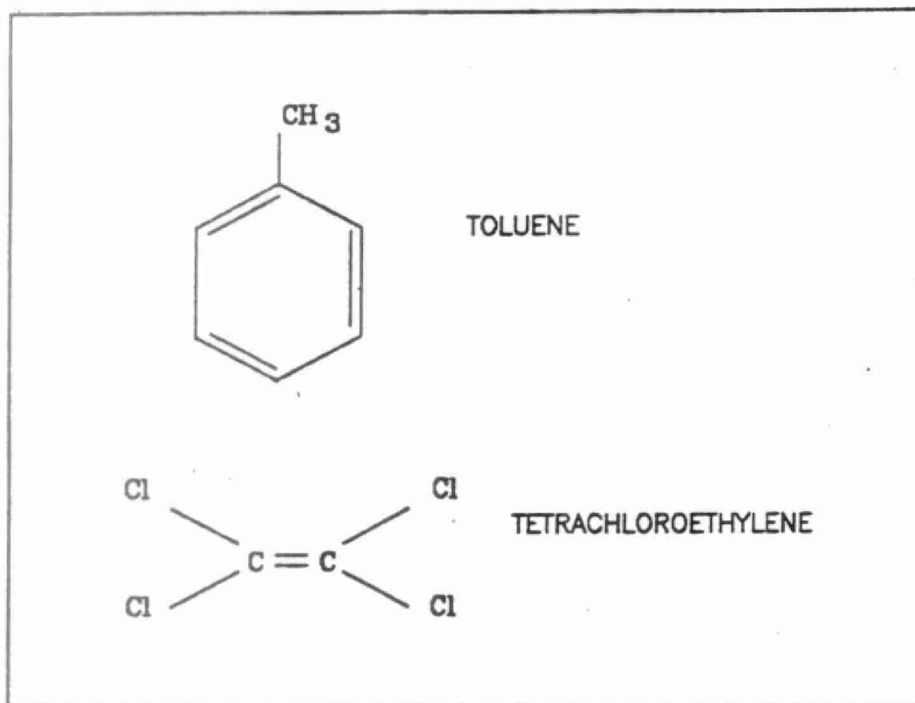
S = solubility

V.P. = vapour pressure

\* Ashworth, *et al.*, (1988).

♥ Handbook of Chemistry and Physics (64th Ed.).

♦ Smith *et al.*, (1980).



**Figure 2.2.** Structural formulas of Toluene and Tetrachloroethylene, taken from Handbook of Chemistry and Physics (64th Ed.)

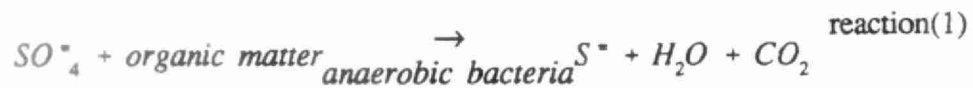
## 2.4 Biodegradation

The conversion of organic compounds to inorganic substances by living organisms is termed biodegradation. It is an essential pathway in the breakdown of organic contaminants in the environment. There are several definitions of biodegradation: primary, ultimate and acceptable. Primary biodegradation is any biologically induced change in the parent compound. Ultimate biodegradation is the conversion from organic to inorganic products (Battersby, 1990). Acceptable biodegradation is the biodegradation to an extent such that toxicity or any other undesirable characteristic of a compound is removed (Handbook of Chemical Property Estimation Methods, 1990). It may be possible for any

of these to be achieved in sewers despite the fact that the time the microbes are exposed to the VOCs would be relatively short.

Many variables can affect the rate of biodegradation. They can be physical such as temperature, pH, moisture, oxygen availability, and the presence of other substances. Other variables may be organism related, such as their spatial distribution, concentration, species composition and degree of acclimation. There are substrate-related variables such as the initial concentration of substrates and their physical and chemical properties. The biodegradation process is sensitive to many environmental conditions (Handbook of Chemical Property Estimation Methods, 1990). It becomes especially complex in a sewer where there is the added difficulty of fluctuating conditions.

Biodegradation in a sewer can be achieved either by suspended microbes in the wastewater or by slime layers attached to wetted walls of sewers. Under appropriate conditions microbes that exist in sewers can be quite active producing large quantities of hydrogen sulphide (USEPA, 1985). The anaerobic autotrophic bacteria in these biofilms form sulphides using sulphate or sulphur containing matter as a terminal electron acceptor to oxidize organic matter. If the dissolved oxygen concentration is less than 0.1 mg/L there will be insufficient oxygen to oxidize all of the sulphide diffusing out of the slime layer. The dissolved sulphides in the wastewater form hydrogen sulphide, a malodorous and very toxic gas. The following reactions show the reduction of sulphate to hydrogen sulphide.



Removal of organic matter in sewers has been indirectly estimated by the measurement of dissolved oxygen (DO) consumption rates (Boon and Lister, 1975; USEPA 1974). Microbial activity in gravity sewers has been monitored by Raunkjaer *et al.*, (1994), who monitored changes in organic matter content during three hours of transportation, and found significant removal of soluble carbohydrate and volatile fatty acids (VFA as acetate). They also determined the removal rate for organic matter under aerobic conditions at 15°C of 20 mg/(L·h) when readily biodegradable compounds were present.

Aerobic heterotrophic biodegradation by suspended and attached biomass in a well mixed-indoor channel was investigated by Cao and Alaerts, (1994). They found the specific activity of the suspended biomass was 50-100% higher than the attached biomass. In their experiments, attached biofilm made a significant contribution to biodegradation when the real wetted area per unit volume of water was large. However this conclusion was only true when the suspended biomass concentration was less than 10 mg/L and the ratio of the wetted area to the volume was equal to 2.1 m<sup>-1</sup>.

Ozer and Kasirga (1994) investigated substrate removal in long sewer lines, using a batch biofilm reactor. They studied suspended and attached growth kinetics to explore the significance of aeration in sewer trunks. They found that for large sewers suspended biomass plays a more important role in the removal of substrate than biofilms, while in small diameter sewers biofilms are more dominant.

#### **2.4.1 VOC BIODEGRADATION**

Little work has been done on the biodegradation of VOCs in sewers. However the biodegradation of VOCs in several controlled environments has been investigated. The degradation of VOCs by various microbes under a variety of conditions has been studied extensively in attempts to aid practical and economical treatment of industrial wastewater.

Kincannon *et al.*, (1983) indicated that in municipal activated sludge treatment plants, biodegradation of some VOCs can occur but volatilization is the primary removal mechanism. They also found that in a laboratory-scale activated sludge reactor, tetrachloroethane, 1,2-dichloroethane and 1,1,1-trichloroethane were completely removed by volatilization but benzene and methylene chloride were removed mainly by biodegradation.

Blackburn *et al.*, (1985) also reported that when they operated a lab-scale activated sludge system under two typical cell retention times, 82 % of toluene was biodegraded while 12 % was volatilized (Namkung and Rittman, 1987).

The fate of VOCs in municipal activated sludge plants was investigated by Parker *et al.*, (1993). They reported that more than 80% of the mass flow of non-chlorinated compounds, (toluene, p-xylene and 4-ethyltoluene) but only 46% of the mass flow of chlorinated compounds, (dichloromethane, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene and 1,4-dichlorobenzene) was biodegraded while the remainder was removed by stripping.

Lewandowski (1990) determined that microbes (mixed liquor) from domestic treatment plants degraded the chlorinated hydrocarbons (2-chlorophenol, 2,6-chlorophenol and 2,4-D) at rates which were virtually the same as those determined from the microbes from the plant that handled industrial waste. Strand *et al.* (1991) used a submerged packed-bed biofilm reactor sparged with air and methane to treat contaminated ground water and determined cometabolic degradation rates of trichloroethylene (TCE) and 1,1,1-trichloroethane. They reported maximum degradation rates of 302 and 400  $\mu\text{g}/(\text{L}\cdot\text{h})$  for TCE and 1,1,1-trichloroethane, respectively.

Biodegradation of VOCs by biofilms has been investigated. Muollo *et al.* (1991) used a silicone-membrane oxygenation system in a fluidized bed reactor, to successfully achieve greater than 95% removal of dichloromethane and toluene. This removal was primarily through biodegradation and was successful for inlet concentrations of up to 61 mg/L of dichloromethane and 16 mg/L toluene in mixed feed.



Debus and Wanner (1992) tested the biodegradation of xylene in a membrane biofilm system. The biofilm grows on the gas-permeable silicone membrane that is supplying the oxygen to the system. They found that all of the xylene in the feed was degraded when the biofilm reached a critical thickness. If the biofilm was smaller than this optimal value the degradation capacity of the biofilm is not sufficient to prevent the transfer of xylene from the liquid to the gas phase. Above this optimal value, the removal rate of the xylene removal decreased because the xylene transport into the biofilm was limited. However the biofilm showed the capability of responding to the fluctuations in the reactor influent in preventing breakthrough of the xylene to the gas phase.

Testing natural biofilms to determine the rate at which they remove trace organics has been reported by Gantzer *et al.*, (1988). They developed a biokinetic model that successfully predicted the rate at which p-cresol and the butoxyethyl ester of 2,4 dichlorophenoxy-acetic acid were removed from their reactor by two types of river biofilms. The biofilm density, thickness and intrinsic microbial rate constants were calculated independently for the first order flux model they used, and the mass transfer parameters were determined from existing equations. The reactor used by the authors was agitated at two different speeds however, no mention was made to any possibility of stripping of the two chemicals.

## MODEL DEVELOPMENT

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There are three mechanisms by which VOCs may be removed from wastewater in sewers. In addition to biodegradation, the other three mechanisms include volatilization, removal by chemical reactions and sorption. Sorption was not considered in this study. Sorption is affected by the water solubility of the contaminant. In general the more hydrophobic the compound the greater the sorption (Bell and Tsezos, 1987). Compared to other pollutants such as poly-aromatic hydrocarbons and pesticides, most VOCs are relatively water soluble. Therefore sorption is not as important a removal mechanism for VOCs as for less soluble compounds (Bell *et al.*, 1992). Furthermore, there is currently a lack of published information related to adsorption kinetics. A general model for the transfer of VOCs across a gas-liquid interface is

$$R_{vol} = K_l a \left( C_l - \frac{C_g}{H_c} \right) V_l \quad (1)$$

where

$R_{vol}$  = rate of gas-liquid mass transfer (mg/s)

$K_l a$  = overall mass transfer coefficient (1/s)

$C_l$  = VOC concentration in wastewater (mg/m<sup>3</sup>)

$C_g$  = VOC concentration in gas phase above the wastewater (mg/m<sup>3</sup>)

$H_c$  = Henry's law coefficient (m<sup>3</sup><sub>liq</sub>/m<sup>3</sup><sub>gas</sub>)

$V_l$  = volume of wastewater (m<sup>3</sup>).

taken from (Corsi *et al.*, 1992).

Biodegradation of organic compounds by suspended biomass in wastewater is typically modelled by a form of the Monod equation in which the rate of biodegradation of a substrate is related to the substrate concentration and microbial biomass (Bell *et al.*, 1992). The Monod equation is typically presented as

$$R_{bio} = \frac{-\mu_m C X_a}{Y' (K_s + C)} \quad (2)$$

where

$R_{bio}$  = rate of substrate (VOC) disappearance ( $\text{g}/(\text{m}^3 \cdot \text{d})$ )

$\mu_m$  = maximum microbial growth rate (1/d)

$C$  = substrate (VOC) concentration ( $\text{g}/\text{m}^3$ )

$X_a$  = active microbial cell concentration ( $\text{g}/\text{m}^3$ )

$Y'$  = cell yield coefficient (g cell/ g substrate)

$K_s$  = half-saturation coefficient, for a substrate (at which specific growth rate is half its maximum value)( $\text{g}/\text{m}^3$ ).

If the substrate concentration is much lower than the half saturation coefficient, equation 2 may be reduced to

$$R_{bio} = -K C X_a \quad (3)$$

where  $K$  is an apparent first order biodegradation rate constant ( $\text{m}^3/(\text{g} \cdot \text{d})$ )

## **EXPERIMENTAL METHODOLOGY: Suspended Biomass**

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### **4.0 ESTIMATION OF MICROBIAL BIOMASS IN SEWER WASTEWATER**

This chapter will discuss the modified procedure that was used to determine the quantity of active biomass in wastewater. It details the materials and methods used to determine the wastewater characteristics.

#### **4.1 COLLECTION OF SAMPLES**

Three sites in the City of Guelph, Ontario were selected for collecting wastewater samples. These were: 1) a residential sewer, 2) a municipal sewer conveying large quantities of industrial discharge and 3) the headworks of a municipal wastewater treatment plant. The residential sewer was located in the heart of a residential area in the northwest-end of Guelph. The wastewater flowed rapidly along this relatively shallow line. The second sewer line that was sampled conveyed wastewater collected from an industrial area. This industrial area was involved in a variety of industries including a hat factory, a textile factory and an electroplating facility. A sample of activated sludge was also collected at the same time from the Guelph wastewater treatment plant. During each collection event, three grab samples were collected at each site and the temperature, dissolved oxygen levels and pH were measured in the field.

## **4.2 WASTEWATER MEASUREMENTS**

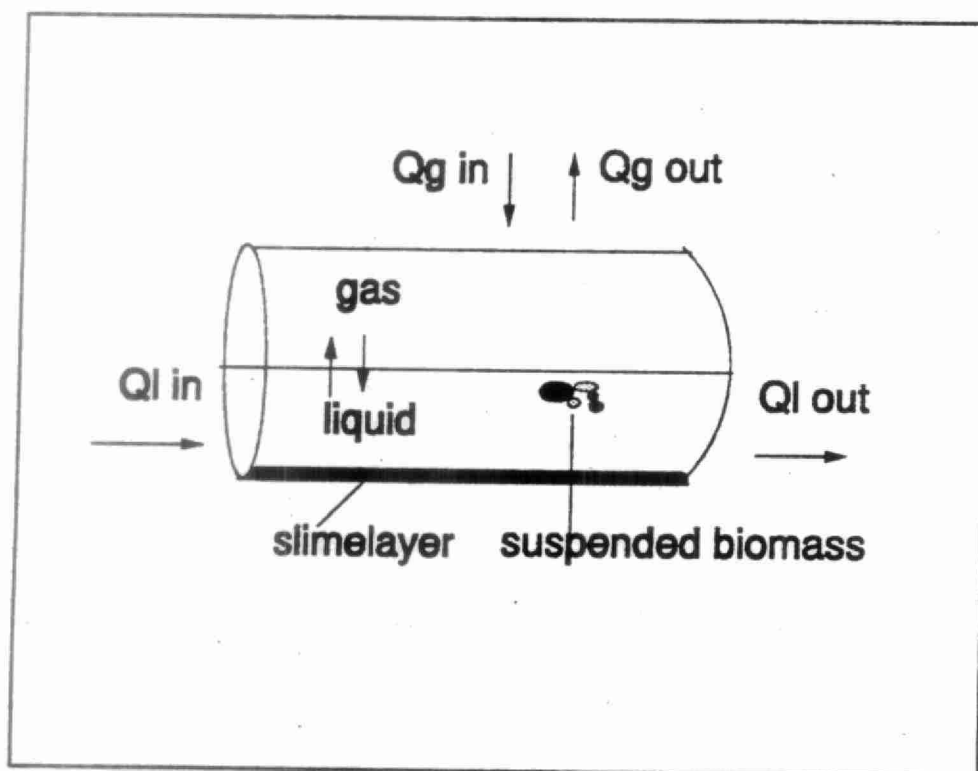
Total suspended solids (TSS), volatile suspended solids (VSS) and chemical oxygen demand (COD) were determined from samples collected in clean 1-L Nalgene bottles. These wastewater samples were placed in an ice chest. Upon return to the laboratory, all samples were kept at 4°C. Samples to be tested for ATP content were collected and immediately frozen in dry ice. Samples were analyzed immediately upon return to the laboratory.

### **4.2.1 Field Measurements**

#### **Dissolved Oxygen, pH and Temperature Measurements**

Dissolved oxygen concentrations were measured using a YSI model #58 oxygen meter and a YSI model 5739 field sampling probe. The dissolved oxygen probe was calibrated each time before use. It was lowered into the sewer and submerged until the DO reading stabilised. The temperature of the wastewater was also measured using the same meter. The pH was measured by taking a sample from the sewer in a small beaker and measuring with a pH meter (Cole-Parmer Chem-det® Model #5850-00), which was calibrated in the field with standard buffer solutions at pH 7 and 10.

Figure 3.1 illustrates a control volume associated with a multi-phase sewer environment.



**Figure 3.1.** Schematic representation of a multi-phase sewer environment

Equations 1 and 3 can be combined in the form of a general mass balance to model the fate of VOCs in sewers. Equations 4 and 5 are the result of a one dimensional differential analysis of liquid and gas control volumes as  $\Delta x$  approaches 0. An expression defining biodegradation by suspended biomass (equation 2) is included in equation 5.

**Gas phase VOC Balance:**

$$\frac{\partial C_g}{\partial t} = -U_l \frac{\partial C_g}{\partial x} + D_g \frac{\partial^2 C_g}{\partial x^2} + K_l a \left( C_l - \frac{C_g}{H_c} \right) \frac{V_l}{V_g} - Q_{gOUT} \frac{C_g}{V_g} + Q_{gIN} \frac{C_a}{V_g} \quad (4)$$

**Liquid phase VOC Balance:**

$$\frac{\partial C_l}{\partial t} = -U_l \frac{\partial C_l}{\partial x} + D_l \frac{\partial^2 C_l}{\partial x^2} - K_l a \left( C_l - \frac{C_g}{H_c} \right) - K_{bio} X_a C_l \quad (5)$$

where

- $C_l$  = liquid concentration of contaminant (mg/m<sup>3</sup>)
- $C_g$  = gas concentration of contaminant (mg/m<sup>3</sup>)
- $C_a$  = ambient (gas) concentration of contaminant (mg/m<sup>3</sup>)
- $t$  = time (s)
- $a$  = specific area (m<sup>2</sup>/m<sup>3</sup>)
- $U_g$  = mean velocity in the gas phase (m/s)
- $U_l$  = mean velocity in the liquid phase (m/s)
- $x$  = spatial coordinate in the direction of flow (m)
- $X_a$  = suspended biomass concentration in the sewer (mg/m<sup>3</sup>)
- $D_g$  = gas-phase dispersion coefficient (m<sup>2</sup>/s)
- $D_l$  = liquid-phase dispersion coefficient (m<sup>2</sup>/s)
- $K_{bio}$  = biodegradation rate constant (m<sup>3</sup>/(mg VOC·s))
- $Q_{gIN}$  = ventilation flow rate into the system (m<sup>3</sup>/s)
- $Q_{gOUT}$  = ventilation flow rate out of the system (m<sup>3</sup>/s)

$V_g$  = gas volume ( $m^3$ )

$V_l$  = liquid volume ( $m^3$ ) , and

$H_c$  = Henry's Law constant ( $m^3_{liq}/m^3_{gas}$ )

An analytical solution of the differential equations 4 and 5 can be derived given the following assumptions.

1. Uniform ventilation of the gas phase; equal amounts of air enter and leave along the entire sewer line and there is no net axial movement of air along the reach. This means in equation 4 the first spatial derivative which describes the bulk flow of the gas phase can be set equal to zero.
2.  $C_g \gg C_a$ , i.e., concentration of the contaminant is greater in the sewer than in the ambient atmosphere. Therefore if  $C_a$  is approximately zero, the last term in equation 4 disappears.
3. Ideal plug flow conditions prevail in the sewer line, so that dispersion is negligible compared to convection in the liquid and gas phase. This means that the second term in both equations 4 and 5 that describe dispersion in the gas or liquid phases respectively, along the sewer line disappears.
4. A steady upstream discharge of wastewater and VOC.
5.  $K_{la}$ ,  $V_l$ ,  $V_g$ ,  $H_c$ ,  $Q_{out}$  and  $K_{bio}$  are all invariant with time.
6. The entire system is at steady state. All the derivatives with respect to time in both equations 4 and 5 can be set equal to zero.



With these assumptions, the equation 4 can be rearranged to yield the algebraic equation:

$$C_g = \frac{K_l a C_l}{\left( \frac{Q_{out}}{V_l} + \frac{K_l a}{H_c} \right)} \quad (6)$$

Substitution of equation 6 into equation 5 and integrating yields the analytical solution:

$$\ln\left(\frac{C_l}{C_o}\right) = \left(-K_l a + \frac{K_l a}{\left(\frac{Q_{out}}{V_l} + \frac{K_l a}{H_c}\right) + 1} - K_{bio} X_a\right) \frac{x}{U_l} \quad (7)$$

where

$C_o$  = liquid concentration of contaminant (mg/m<sup>3</sup>) at time,  $t = 0$ .

The stripping and partitioning process is described by the first two terms and biodegradation by the last term on the right hand side of equation 7. Equation 7 was incorporated into a computational spreadsheet to compare volatilization and biodegradation. It is discussed further in chapter 6.

The measured VOC concentrations in municipal sewers measured are quite low. VOCs concentrations in raw wastewater entering a WWTP are typically measured at concentrations in the range of 1 to 100 µg/L (Bell *et al.*, 1992; Parker *et al.*, 1993). Therefore the use of equation 3 would be appropriate.

To model biodegradation by suspended biomass in a wastewater collection system, the two parameters that are most difficult to interpret are the active microbial concentration and the biodegradation rate constant. In activated sludge systems, the active microbial biomass is generally considered to be the mixed-liquor volatile suspended solids (MLVSS) (Metcalf and Eddy, 1991). In a sewer, the fraction of volatile suspended solids (VSS) that represents active biomass is much less than that in an activated sludge reactor.

There is a lack of experimentally determined kinetic constants (K) for VOCs in the literature. Most of the experimental data related to K for VOCs are based on laboratory scale bio-reactors, involving fully acclimated microbial populations. The use of these values is likely to lead to over-estimation of biodegradation for sewers.

#### **4.2.2 Laboratory Analyses**

##### **4.2.2.1 Chemical Oxygen Demand (COD)**

The COD of each sample was measured using closed reflux colorimetric method, 5220D as described in Standard Methods for the Examination of Water and Wastewater (17th Ed.). Two grab samples were collected and two replicates of each sample were tested to determine the COD. A Milton Roy spectronic 20 D spectrophotometer was used for spectral determination.

##### **4.2.2.2 Suspended Solids**

The TSS and VSS were determined by using methods 2540D and 2540E, respectively, described in the Standard Methods Handbook for the Examination of Waste and Wastewater (17th Ed.). Glass fibre filters (Whatman 934-AH) and aluminum sample trays were used. Two grab samples were taken from the sewer and three replicates of each sample were tested for TSS and VSS content.

#### **4.3 ADENOSINE TRIPHOSPHATE (ATP) ANALYSIS.**

Determining total ATP content is one of several methods of estimating microbial biomass. It has been used to estimate biomass levels in soil (Fairbanks *et al.*, 1984), in sewage sludge compost (Lehtokari *et al.*, 1983), in activated sludge and

in wastewater (Jorgenson *et al.*, 1992; Neethling *et al.*, 1988; Patterson *et al.*, 1970; Roe *et al.*, 1982). It is also a standard method for the determination of plankton biomass. Adenosine triphosphate is found in the protoplasm of all metabolising cells. It has a very short survival time following cell death, and can be used as an indicator of the number of viable organisms.

Biomass concentrations in sewers were estimated using an ATP assay. The ATP concentration of biomass in sewers must be related to some standard because it has not been extracted from a pure culture. Activated sludge consisting of a mix of bacteria was the standard to which the ATP concentration of sewer biomass was related. The types of biomass in raw wastewater entering a treatment plant can have a considerable influence on the total composition of biomass in the activated sludge process (Henze, 1986).

Biodegradation rate constants for VOCs determined in activated sludge reactors are given in terms of mixed liquor volatile suspended solids (MLVSS). Therefore to use these rate constants to estimate the biodegradation of VOCs in sewers requires that the estimate for the amount of biomass in a sewer be determined in terms of MLVSS.

The ratio of ATP in raw wastewater to the ATP in activated sludge was taken to be indicative of the ratio of active biomass in a sewer to that in an activated sludge reactor. Using the mixed-liquor volatile suspended solids (MLVSS) as an estimate of

active biomass in an activated sludge reactor, we can estimate the active biomass in the sewer by using the following equation:

$$\frac{ATP_{sewer}}{ATP_{activated\ sludge}} * MLVSS_{activated\ sludge} = MLVSS_{sewer} \quad (8)$$

The estimates for the MLVSS in the sewer are conservative, since the MLVSS of the activated sludge is not 100% active biomass.

#### 4.3.1 Sample Calculation of Biomass Estimates

The following example shows the calculation of the amount of biomass in terms of MLVSS for industrial wastewater collected on the 11th of February 1993.

MLVSS activated sludge = 2240 mg/L

Average ATP in Industrial wastewater =  $7.67 \times 10^{-6}$  µg/ml

Average ATP in activated sludge = 0.896 µg/ml

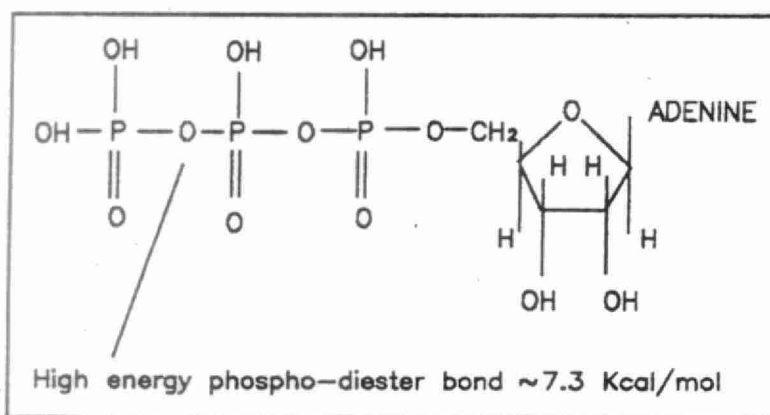
$ATP_{sewer}/ATP_{asludge} = 8.56 \times 10^{-7}$

Using equation 8

$MLVSS_{sewer} = 8.5 \times 10^{-7} \times 2240 \text{ mg MLVSS/L} = 0.024 \text{ mg MLVSS/L}$

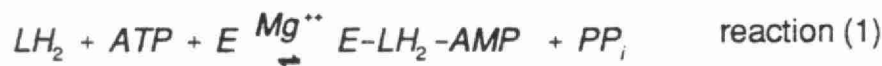
### 4.3.2 Theory

Adenosine triphosphate is a major source of chemical energy used by all cells. It is the means by which cells temporarily store energy derived from nutrients. This energy can eventually be used for cellular activities such as transport and biosynthesis. Adenosine triphosphate is formed by the linkage <sup>through a</sup> of high energy phospho-diester bond to adenosine diphosphate (ADP).



**Figure 4.1.** Structure of ATP

Adenosine triphosphate concentration is measured by bioluminescence. Light production in fireflies is caused by luciferin (LH<sub>2</sub>) reacting with ATP in the presence of the enzyme luciferase (E), oxygen and magnesium ions (Lundin and Thore, 1972).



Luciferin in the presence of ATP and magnesium ions forms a reversible enzyme luciferin-AMP complex (luciferyl adenylate) and pyrophosphate (reaction 1). The complex is then rapidly and irreversibly oxidized to oxy-luciferyl adenylate in an excited state (reaction 2). This excited state is followed by release of a quantum of light (reaction 3). The ATP concentration is directly proportional to the light output. The light is observed as luminescence and can be monitored by a scintillation counter or photometer.

#### 4.3.3 Materials and Method for ATP Analysis.

Adenosine triphosphate analysis is rapid, and can be completed in less than one hour. Sigma® chemicals provided the bioluminescent kit (Stock No. FL-AA) for ATP determination. It consisted of lyophilized disodium ATP salt to make up standards for the calibration curve. The luciferin-luciferase enzymes were provided in an ATP assay mix that contained magnesium sulphate and ethylenediamine tetra-acetic acid (EDTA) in a Tricine buffer. A dilution buffer was provided for diluting the enzyme.

To ensure reproducibility, a low background light emission and maximum sensitivity the following precautions were carried out before use. All components of the kit were reconstituted using sterile distilled water. All glassware used was soaked overnight in 1N HCl and permitted to air dry.

#### 4.3.3.1 ATP Extraction

The following procedure was adapted from Neethling *et al.*, (1988), to extract ATP from activated sludge and wastewater. The ATP was extracted using 20 mM Tris [tris(hydroxymethyl)aminomethane] buffer plus 2mM ethylenediamine tetra-acetic acid (EDTA), pH 7.75. Five millilitres of activated sludge was diluted 10 fold with Tris buffer while the raw wastewater was not diluted. Ten millilitres of boiling (Tris/EDTA) buffer was added to 2 millilitres of the diluted activated sludge or raw wastewater. This mixture was boiled for 90-120 seconds, cooled rapidly on ice and centrifuged at 3000 rpm for ten minutes to remove debris. Then, 200  $\mu$ L portions were frozen in plastic vials at -20 °C until ATP measurement.



#### 4.3.3.2 Light Measurement

The light output from the extract was measured by a Chem-glow Photometer which was designed to make quantitative determinations of bio- or chemi-luminescent reactions. This photometer was attached to a strip chart recorder and it can detect as low as  $10^{-13}$  g ATP/ml. The quantity of light emitted was measured by integration of the light signal over 10 seconds, after a 6-second delay.

The ATP assay mix (0.1 millilitre) was placed in a cuvette and rapidly swirled and permitted to stand for 3 minutes to reduce the background emission. Either the standard or sample (0.1 millilitre) was then rapidly added to the cuvette, swirled and placed in the photometer to measure the light output. To determine the amount of background light produced, it is necessary to run blanks. The above procedure was carried out but instead of the sample or standard, Tris buffer was added. The light output of the Tris buffer was subtracted from that of the sample. This final value is proportional to the amount of ATP in a sample. A similar procedure was carried out for the ATP standards using sterile water.

The light output data of the standards was used to plot the calibration curve required (relative light intensity versus ATP concentration). The light output from the samples of wastewater and activated sludge was used with this calibration curve to determine ATP concentrations.

## RESULTS: Suspended Biomass

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### 5.1 ATP ANALYSIS

The results for the suspended biomass experiments are presented in Tables 5.1 and 5.2. Table 5.1 presents the results of TSS and VSS analysis. It also indicates ATP recovered and activity measurements for the ATP analysis. The calibration curves for ATP determinations are presented in Appendix A. The R squared values are good in general, ranging from 0.86 to 0.99.

The TSS, VSS and COD values exhibited variation within and between sampling events. However, they were in general within the ranges expected for municipal wastewater. The calibration curve for the COD experiments had R squared values that ranged from 0.825-0.899 (these are available in Appendix A). The dissolved oxygen levels in all experimental sewers were quite high, ranging from 8.4 mg/L in a residential sewer to 4.2 mg/L in an industrial sewer line. These values indicated that the wastewater in the sewer was capable of sustaining aerobic activity.

The concentration of ATP in the activated sludge ranged from 0.9 to 1.4  $\mu\text{g}/\text{ml}$ . These are similar to the range of ATP values noted by Joregenson *et al.*, (1992), from activated sludge, 1.2  $\mu\text{g}/\text{ml}$  to 4.2  $\mu\text{g}/\text{ml}$ . Roe *et al.*, (1982), in their activated sludge viability studies found higher ratios of 5.51  $\mu\text{g}$  ATP/mg SS. These ratios are an order of magnitude larger than those determined by Joregenson *et al.*, (1992) and this author.

Roe *et al.*, (1982) attributed the high values to two facts; first they used a hot sand bath which is more efficient in extracting ATP from cells than the boiling water bath used to heat the Tris buffer to boiling as done by other researchers and second to the fact they measured the sludge at maximum viability.

A trend was noted in the ATP content from various locations. Wastewater collected from industrial and residential sewers had less ATP/g VSS than that taken from the headworks of the wastewater treatment plant, which had less than the activated sludge. This general trend can also be observed in data presented by Joregenson *et al.*, (1992). The activated sludge ATP content in this study is similar, however the ATP content in the wastewater is lower than those presented by Jorgenson *et al.*, (1992).

Estimates of biomass concentration using ATP analysis are presented in Table 5.2. Biomass concentrations were significantly lower than the VSS and ranged from 0.02 mg MLVSS/L to 19 mg MLVSS/L.

As expected, the biomass concentrations in the industrialized reach were generally lower than those in the residential reach or the plant head works. Industrial wastewater will receive a variety of toxic chemical slugs more frequently than residential sewers. Only a very small fraction of suspended biomass will survive the variety and frequency of these toxic slugs. In industrial wastewater there is not a large amount of human waste to provide the initial bacteria that would provide the seed from which biomass could grow.

Biomass concentration in general appeared to be two orders of magnitude higher in headwork samples compared to samples from the sewer lines. The raw wastewater at the headworks was a mix from several sewers. This means that this raw wastewater entering the treatment plant could be a mix of high, medium and low strength wastewaters. Depending on the relative amounts of suspended biomass in each contributing sewer the suspended biomass levels can be expected to be higher or lower than those found in individual sewers. The microbes that arrive at the headworks have had time to grow and multiply. The wastewater flow has also sloughed the walls of the sewers, on the way to the treatment plant, removing any loose slime layers; this would also contribute to the increased biomass observed in the raw wastewater at the headworks.

Biomass concentrations represent a small fraction of the total VSS in sewers. These results will be used to estimate biodegradation rates associated with suspended biomass in sewers, with the intent of comparing the relative importance of such biodegradation with VOC losses caused by gas-liquid mass transfer.

Table 5.1 Suspended solids and ATP measurements

DATE/REACH	TSS mg/L ± SD	VSS mg/L ± SD	ATP µg/ml ± SD	ATP content µg ATP/ g VSS
Feb 11/93 industrial residential headworks sludge	72 ± 8.4 110 ± 15 155 ± 37 2960 ± 110 n = 6	70 ± 10 113 ± 24 121 ± 19 2240 ± 105 n = 6	8x10 <sup>-6</sup> ± 1.8x10 <sup>-6</sup> 5x10 <sup>-5</sup> ± 3.7x10 <sup>-5</sup> 0.007 ± 0.0016 0.9 ± 0.005 n = 3	0.11 0.44 58 400
Feb 18/93 headworks sludge	176 ± 46 2740 ± 32 n = 6	146 ± 37 2120 ± 258 n = 6	0.02 ± 0.006 3.5 ± 0.022 n = 3	140 240
March 2/93 industrial residential headworks sludge	208 ± 23 106 ± 11 220 ± 100 2240 ± 350 n = 6	183 ± 21 94 ± 5 188 ± 67 1700 ± 249 n = 6	8x10 <sup>-5</sup> ± 4.1x10 <sup>-5</sup> 1x10 <sup>-4</sup> ± 2.0x10 <sup>-5</sup> 0.006 ± 0.003 1.3 ± 0.003 n = 3	0.44 1.1 32 760
March 9/93 industrial residential headworks sludge	78 ± 27 136 ± 39 238 ± 67 3420 ± 117 n = 6	67 ± 21 108 ± 36 198 ± 65 2810 ± 136 n = 6	3x10 <sup>-4</sup> ± 6.5x10 <sup>-6</sup> 3x10 <sup>-5</sup> ± 0.0001 0.009 ± 0.002 1.4 ± 0.004 n = 3	4.5 0.27 45.5 500

**Table 5.2. Biomass estimates and wastewater characteristics**

Date/Reach	Biomass mg MLVSS/L ± SD	pH	Temp °C	DO mg/L	COD mg/L
February 11 industrial residential headworks	0.02 ± 0.0051 0.13 ± 0.11 19 ± 1.8	8.3 8.4 8.4	9.1 10.0 12.1	4.2 4.9 7.5	81-145 250-530 390-350
February 18 headworks	13 ± 3.4	8.5	12.1	7.8	290-650
March 2 industrial residential headworks	0.10 ± 0.05 0.14 ± 0.03 8.0 ± 3.7	6.4 8.8 8.1	11.5 12.1 10.3	6.4 6.2 6.2	710-800 530-580 450-520
March 9 industrial residential headworks	0.05 ± 0.01 0.50 ± 0.20 14.5 ± 3.4	6.6 6.8 7.6	11.1 13.7 12.5	5.4 8.4 8.5	450-460 540-690 140-240

## MODEL ANALYSIS

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### 6.1 MODEL CHARACTERISTICS

Equation 7, presented in chapter 3, was incorporated in a computational model. This model can be used to calculate the amount of contaminant remaining at the end of a specific reach and the percentage of compound that was stripped and biodegraded. A 5 km reach was chosen for this analysis.

The physical sewer characteristics were chosen from experimental reaches in Davis and in Sacramento used by Corsi *et al.*, (1992) in previous VOC emission studies. The Parkhurst and Pomery, (1972) model for oxygen transfer in sewers was used to estimate the mass transfer coefficient for oxygen.

$$K_{o_2} = 2.67 \times 10^{-4} (1 + 0.17 F^2) \tau (S U)^{3/8} \quad (9)$$

Where

- F = Froude number (-)
- $\tau$  = temperature correction factor (-)
- $K_{o_2}$  = overall mass transfer coefficient for oxygen (m/s)
- S = slope of the energy gradient (m/m)
- U = mean velocity of the wastewater (m/s)

This mass transfer coefficient for oxygen can be adjusted by multiplying it by  $\Phi$ , the ratio of the VOC to oxygen liquid-phase mass transfer coefficients. It generally ranges from 0.5 to 0.7 in natural surface waters and wastewater (Smith *et al.*, 1980). In this case a  $\Phi$  of 0.5 was used to estimate  $K_a$  for toluene.

## 6.2 VIABLE BIOMASS

A set of conditions were chosen (Table 6.1) to observe the results of varying the magnitude of  $X_v$ , the amount of viable biomass in sewers using the estimates determined from the ATP experiments. The total ATP content provided a method of estimating only the living biomass. The VSS of wastewater which is typically used as an indicator of biomass in wastewater includes dead biomass and other non living materials such as paper that can be found in sewer wastewater. Values of 0.1, 1 and 20 mg/L were chosen since the biomass in both residential and industrial sewers was generally  $< 1$  mg/L and 20 mg/L was the largest biomass observed.

A biological rate constant for the biodegradation of toluene of  $0.4 \text{ m}^3/(\text{g MLVSS} \cdot \text{d})$  was taken from, Namkung and Rittman, (1987). The  $K_a$  for toluene in the sewer was estimated to be  $0.000207 \text{ s}^{-1}$ .



**Table 6.1 Contaminants and sewer characteristics used in the model.**

Contaminant Characteristics		Sewer Characteristics	
Toluene		Diameter(m)	0.5
$H_c \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$	0.23	Slope (m/m)	0.005
$K_{\text{bio}}$ ( $\text{m}^3/\text{gMLVSS}\cdot\text{s}$ )	$4.6 \times 10^{-6}$	Roughness	0.014
Initial concentration ( $\text{mg}/\text{m}^3$ )	100	Length of pipe (m)	5000
		Temperature (K)	293

**Table 6.2 Model predictions for VOC removal along a 5-km reach by stripping and biodegradation for three different biomass concentrations**

	Case 1	Case 2	Case 3
Vent rate (m <sup>3</sup> /s)	0.11	0.11	0.11
X <sub>a</sub> (g MLVSS/m <sup>3</sup> )	0.1	1	20
K <sub>1a</sub> (1/hr)	0.74	0.74	0.74
Depth (m)	0.15	0.15	0.15
Removal %	66	69	97
% stripped	99	90	32
% biodegraded	1	10	68

When X<sub>a</sub>, viable biomass was 1 mg/L there was practically no removal of toluene by biodegradation. Most of the removal along the reach was via stripping. At 20 mg/L it appeared that 97 % of the toluene was removed along the sewer and 68 % of the removal was by biodegradation. However, at 1 mg/L there is 69 % removal

along the reach and 90 % was removed via stripping. At even lower concentrations the total removal remains close to 69% but only 1 % of the removal is due to biodegradation. These are very conservative estimates of the affects of biodegradation as the biodegradation rate constant for toluene is for acclimated activated sludge. Futhermore, viable suspended biomass concentrations of 20-100 mg MLVSS/L are unlikely in most municipal sewers.

The biodegradation rate constant for the breakdown of toluene by acclimated activated sludge is not appropriate for use in modelling the biodegradation of toluene in a sewer line. Therefore reactor experiments were required to acquire a better estimate for toluene biodegration by wastewater and the slimelayers in the sewer.

## EXPERIMENTAL METHODOLOGY: Biofilms

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### 7.1 EXPERIMENTAL DESIGN

A batch reactor design was chosen to assess the significance of fixed film biodegradation as a VOC removal mechanism in sewers. The slime layers in municipal sewers would only be exposed to VOCs in batches for relatively short periods of time, whereas those in industrial sewers may be exposed for longer periods of time. Three reactors were constructed, a control and two experimentals. Stainless-steel tags coated with slime layers were placed in these reactors. The control and experimental reactors were chosen randomly. Medical-grade compressed oxygen, (a least 99.5% pure, Canox) was supplied to the reactors using Gortex tubing. This Gortex tubing is constructed of 100% polytetrafluoroethylene (PTFE) approximately 1 mm thick, it had an internal diameter of 5.4 mm. This tubing was 77% porous with 1-3  $\mu\text{m}$  pores, that permit oxygen to diffuse into the water without bubbling. In general PTFE is inert to all chemicals except molten alkali metals, fluorine and certain complex halogenated compounds at elevated temperatures and pressures (Technical Manual, Fluoroware). Therefore this tubing would not absorb VOCs and hence stripping of the VOCs from the liquid in the reactor was prevented.

Oxygen was supplied at a pressure of 6 inches of water. Several brief experiments were carried out to determine the mass transfer coefficient ( $K_a$ ) for the Gortex tubing. The mass transfer coefficient of the Gortex tubing using clean water was determined to be  $0.0002 \text{ min}^{-1}$ .

Forty stainless-steel tags, each 80 mm long, and 39 mm in diameter were constructed. Two batches of ten tags were suspended by nylon rope in the manhole of the Massey Creek interceptor (MCI) sewer. The MCI sewer is located in the greater Toronto area. It conveys industrial wastewater that contains substantial quantities of solvent discharges. The physical characteristics of the reach included a total length of 1.6 km, channel slopes ranging from 0.25 -1.0% and pipe diameters ranged from 0.9m to 1.2m. In the 0.25 % channel slope section, when the MCI is half full the wastewater has a flow rate of  $0.4 \text{ m}^3/\text{s}$ . The walls of the sewer, particularly the section surrounding the manholes, were heavily coated in a grey/brown slime. The tags were rubbed against the sewer wall so that they were lightly coated in the slime and suspended in the air space of the sewer. Unfortunately, not much of a slime layer grew on the tags. Therefore, when slime layers from MCI were to be used in an experiment a clean Ziploc bag was filled with scrapings of slime layers from the tags and the sewer walls. The Ziploc bag was then placed in a cooler and transported back to the laboratory and stored at  $4^\circ\text{C}$ .

The other twenty tags were suspended using either nylon rope and metal chain in the head works of the GWWTP. Stainless-steel tags which were placed in the headworks for a minimum of two months and had with visible growth upon them were used in all

the experiments. When tags were required for an experiment they were removed from the sewer and suspended from the lid of a 2-L glass jar filled with wastewater. The samples were kept in an ice chest, returned to the lab and refrigerated at 4°C. Scrapings were also taken from the walls of the headworks. The scrapings were placed in a glass jar and kept in an ice chest, and upon return to the lab also refrigerated at 4°C.

The dissolved oxygen (DO) concentration was measured using a Model 58 YSI dissolved oxygen meter, using 3-millilitre samples taken periodically throughout the experiment. The temperature and pH were measured using a model 5986-60 Chemdet pH-meter.

Wastewater was placed in the reactors and held at 20°C after being injected with the VOCs in question and mixed using teflon covered magnets for three hours before taking the first sample. Immediately, thereafter the stainless steel tags with slime layers were placed in the reactor. Duplicate samples were collected at intervals for the duration of the experiment and analyzed immediately. Once a sample was removed it was replaced by the same volume of sterile, deionized water to maintain the same headspace in the reactors throughout the experiment.

## 7.2 REACTOR CONSTRUCTION

Figure 7.1 shows a schematic of the experimental reactor design. Each reactor was constructed from a 2-L glass jar with a teflon-lined lid. Four holes were drilled into each of the lids, for the insertion of a manometer, injection/sample port, an oxygen supply and a stainless steel hook from which the stainless steel tags were suspended. The injection/sample port contained teflon lined septa to prevent sorption of the VOCs.

The reactors were stirred magnetically at 400 rpm using teflon covered magnets. Two reactors were each driven by a Fisher-Scientific model #11-500-79 magnetic stirrer and the third reactor by a Cole-Parmer model 04639-30 magnetic stirrer. The lids of the reactors were replaced after having been used three times. The lids were cleaned with Javex bleach and dried in a drying oven overnight and wiped with ethanol and air dried before reuse.

Gortex tubing was used to supply oxygen to the wastewater. It permitted oxygen to diffuse into solution while not permitting VOCs to sorb onto its surface. In each reactor, six inches of Gortex tubing was attached to the oxygen supply and the other end sealed using a stainless-steel clamp.

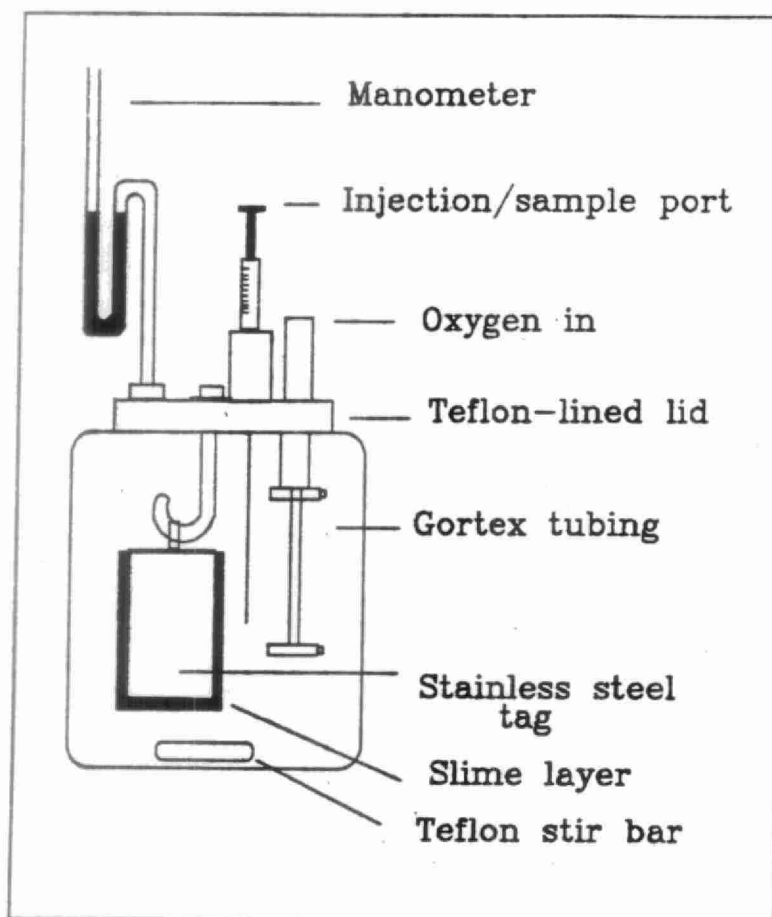


Figure 7.1 Schematic of the Reactor

## 7.3 ANALYSIS

### 7.3.1 VOCs

The volatile mixture which was initially made up for injection into the reactor was also used to make serial dilutions for VOC standards. A new set of VOC standards was analyzed at the beginning of every experiment. To make the injection standard, 0.2 millilitres of toluene and/ or 0.06 millilitres of tetrachloroethylene was dissolved in 10 millilitres of methanol. One millilitre of this mixture was injected into the reactor to



obtain a final concentration of approximately 10 mg/L of toluene and 5 mg/L of tetrachloroethylene. Seven experiments were also carried out using an initial concentration of 1 mg/L of toluene in the reactors. The injection standard for these experiments were made up by injecting 0.02 millilitres of toluene into 10 millilitres of methanol. One millilitre of this mixture was then injected into the reactors to achieve a final concentration of approximately 1 mg/L.

To prepare the rest of the VOC standards, 0.10 millilitre of the injection standard was dissolved in 10 millilitres of water. Serial dilutions of this standard were made so that a range of concentrations from 35 mg/L to 0.086 mg/L was obtained for the 10 mg/L concentration of toluene. The standards for the 1 mg/L toluene concentration ranged from 3.5 mg/L to 0.0086 mg/L, and for PCE from 19 mg/L to 0.9 mg/L.

Duplicate samples of wastewater were collected from each reactor at set intervals. They were placed in 10-millilitre glass vials with teflon-lined septa, and shaken on a LabLine Multi-Wrist hand shaker for 10 mins. They were then placed in the Hewlett-Packard model 19395a headspace sampler. The samples were permitted to equilibrate for 105 minutes before a sample of the headspace in the first vial was injected into the Hewlett-Packard 5890 Series 11 gas chromatograph with a flame ionization detector. Table 7.1 shows the settings used by the headspace sampler and the gas chromatograph.

### 7.3.2 Biofilm Analysis

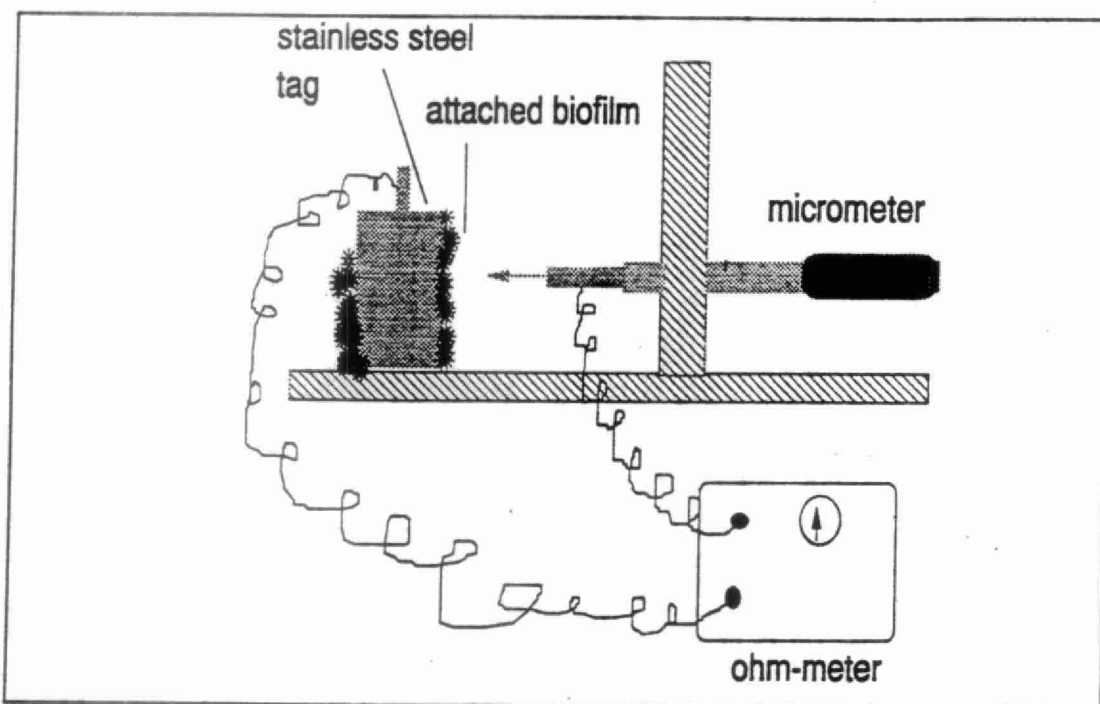
#### 7.3.2.1 Thickness

The thickness of the slime layer was measured using a device constructed for this purpose at the end of an experimental run. A schematic of the apparatus is shown in Figure 7.2. This technique is a slight variation of one outlined by Characklis and Marshall (1992). The apparatus measures the wet thickness of the biofilm by electrical conductance. It is a micrometer with a stainless-steel needle attached. This needle and the stainless-steel tag form an electrical circuit when connected to an ohm-meter.

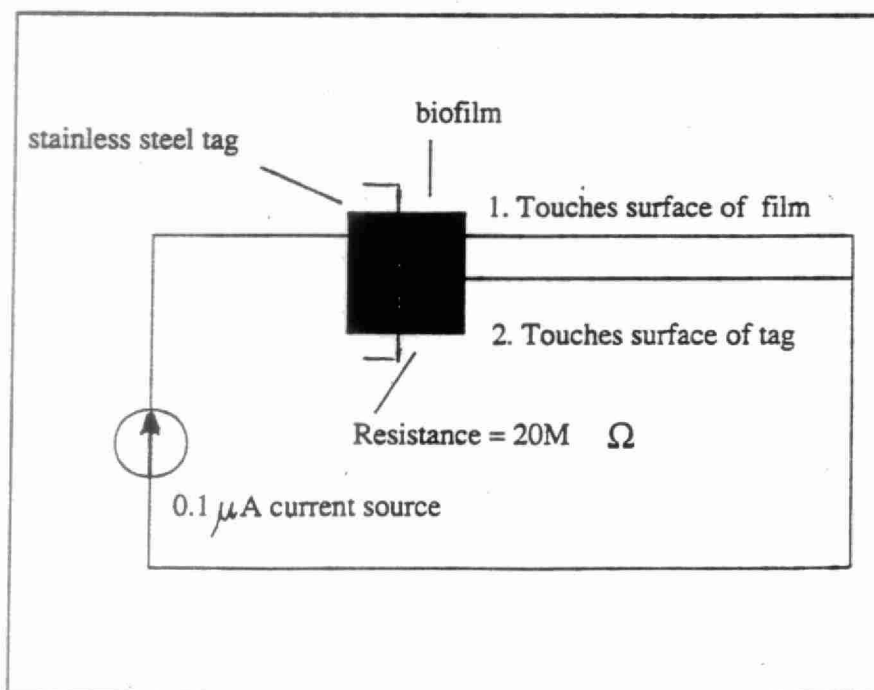
The ohmmeter used was a Hewlett-Packard model HP3425 digital multimeter which can detect high resistances on the order of 20M ohms. The needle was extended to the surface of the biofilm where a spike of current indicated a resistance that was displayed on the ohm-meter. The micrometer reading was noted and then adjusted until the needle touched the stainless-steel tag and completed the circuit, at this point the resistance was zero. The difference in the micrometer readings was the biofilm thickness. Eight readings were taken from each tag. The surface of the tag was divided into four quadrants and two readings were taken from each quadrant, one above the midpoint of the tag and the other below. A circuit schematic is provided in Figure 7.3.

**Table 7.1 Operating conditions for the gas chromatograph and the headspace sampler (HSS) a model HP5890 Series 11, capillary inlet (Split), FID**

HSS CONDITIONS		GC CONDITIONS	
Headspace method	1	Inlet temperature	250°C
Equilibration time	105 min	Oven temperature	initial 30°C, 6 mins. Ramp 10°C/min to 150°C.
Bath temperature	65°C	FID temperature	250°C
Valve/loop temp	65°C	Column	
Sampling interval	34 min	Part No Dimension	30mm x 0.32mm ID
		Stationary phase	DB-5
Aux pressure	1.6 bar	Flow rates	
Carrier flow (He)(HSS only)	30 ml/min	Column (He)	2 ml/min
		Aux. gas	71.9 ml/min
		Splitflow	50 ml/min
		Septum Purge	6 ml/min
		Air	450 ml/min
		Hydrogen	75.9 ml/min



**Figure 7.2.** Schematic of the biofilm thickness measuring device



**Figure 7.3.** Circuit schematic for the biofilm measuring device

#### 7.3.2.2. Volatile Suspended Solids (VSS) content of the wastewater

The VSS of the wastewater was taken from the Guelph Water Pollution Control Monthly Statistics. Guelph wastewater treatment plant (GWWTP) measure the influent VSS to the plant every day. In appendix B, Table B-1 shows the dates on which experiments were carried out and the VSS of the raw wastewater.

#### 7.3.2.3 Biofilm Density and Volatile Suspended Solids content.

A known area on the stainless steel tag was scraped and the wet weight of the biofilm was measured. The dry weight and the VSS content of the biofilm were determined. The biofilm was dried at 103°C, for 60 minutes, cooled in a dessicator until the weight loss was less than 0.5 mg between readings. The dried biofilm was burned in a muffle furnace at 550°C to determine the VSS. The surface concentration of biomass on the tag (B) was calculated by dividing the volatile solids content of the dried biofilm by the scraped area of the tag (A).

$$B = \frac{VSS}{A} \quad (10)$$

Where

B = surface concentration of biomass on tag (mg VSS/cm<sup>2</sup>)

VSS = volatile solids portion of biomass (mg VSS)

A = scraped area on tag (cm<sup>2</sup>)

The density of the biofilm  $X_b$  was determined for the biofilm coated tags growing in the headworks of the GWTTP. The value of  $X_b$  was determined from the following equation

$$X_b = \frac{B}{L_t} \quad (11)$$

where

$X_b$  = biofilm density (mg/cm<sup>3</sup>)

$L_t$  = thickness of the biofilm (cm)

## RESULTS: Reactor experiments

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### 8.1 BIOFILM VOLATILE SUSPENDED SOLIDS

Table 8.1 presents the results of the analysis of the six biofilm coated tags which were representative of those used in the reactor experiments. All the tags were hung just after the bar racks at the headworks of the GWWTP.

**Table 8.1 Biofilm data**

Percent water in biofilm  ± SD	Average measured thickness mm ± SD	Biofilm density mg VSS/cm <sup>3</sup> ± SD	Average mg VSS/cm <sup>2</sup> ± SD
72 ± 3.0 n = 6	0.29 ± 0.1 n = 6	25.1 ± 5.3 n = 6	0.75 ± 0.3 n = 6

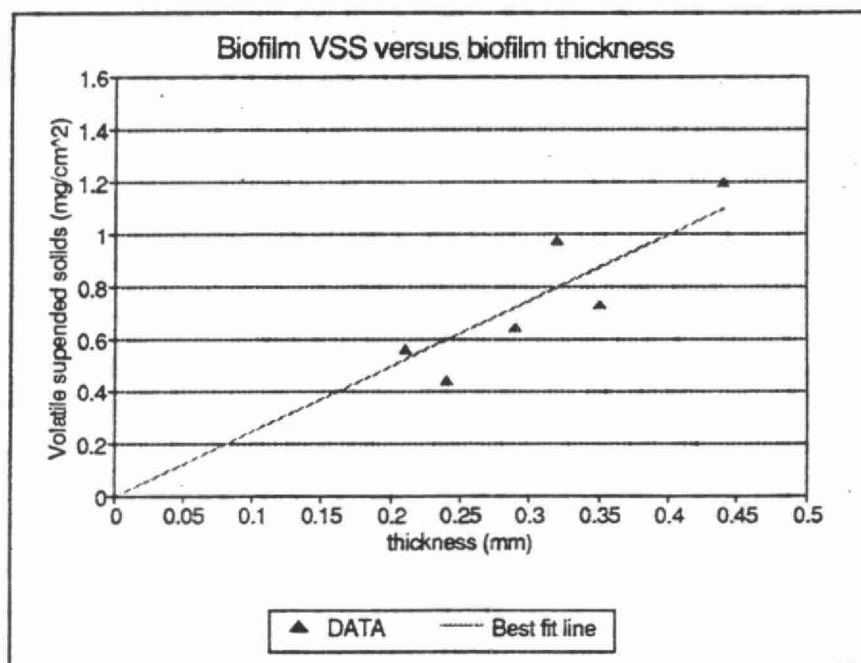
Biofilms were generally assumed to be 99% water (Rittman and McCarty, 1980). For this study, biofilms which grew on tags hung in the headworks of the Guelph treatment plant contained only 72 % water. Biofilms generally have a base layer above which active layers grow. The tags used were constructed from smooth stainless steel, and because of this smooth texture, the stainless steel was not amenable to biofouling. Therefore it is possible that a very thick layer of inert material was formed before the active layer developed.

The biofilm grew in grey-black, mucoid-like patches on the tags and were in general about 290  $\mu\text{m}$  thick. Typically slime layers in sewers range from 0.3-1.0 mm in thickness (USEPA, 1985). The thickness of the slime layer on the tags could be affected by the varying conditions at the treatment plant such as wastewater velocity, influent VSS and the abrasive quality of the wastewater.

The average concentration of biofilm on the six tags was  $0.75 \pm 0.3 \text{ mg VSS/cm}^2$ . The average density of the six biofilms was  $25.1 \text{ mg VSS/cm}^3$ . Gantzer *et al.*, (1992) reported surface concentrations ranging from 0.095 to  $0.560 \text{ mg VSS/cm}^2$  for pond and river biofilm grown on Teflon strips. Their biofilm density ranged from 29.1 to  $14.1 \text{ mg VSS/cm}^3$ . Cao *et al.*, (1993) reported a concentration of  $1.4 \text{ mg VSS/cm}^2$ , for a biofilm grown on polypropylene strips in a trickling filter treating domestic wastewater. The density of the biofilm grown on polypropylene strips was  $18.7 \text{ mg VSS/cm}^3$  which is comparable to those reported by Hickey (1988), who reported a range of values of the biofilm concentration for a variety of river sewage fungus biofilm ranging from  $0.85 \text{ mg Carbon/cm}^2$  for a filamentous type biofilm to  $8.5 \text{ mg Carbon/cm}^2$  for a thick one. The densities of these river sewage fungus biofilms were much smaller, ranging from  $1.7 \text{ mg Carbon/cm}^3$  to  $10.2 \text{ mg Carbon/cm}^3$ . The benthic river sewage fungus biofilms were much thicker and less compact, than those utilized by Cao *et al.*, (1993), Gantzer *et al.*, (1992) and the author.



The concentration of biofilm on the tags varied with biofilm thickness. A graph of biofilm VSS in  $\text{mg}/\text{cm}^2$  versus thickness was plotted (see Figure 8.1) and a linear regression was carried out on the data. This was done since the biofilm thickness on each tag used in a reactor experiment was measured, but a VSS content was not carried out on the biofilm in every experiment. Once the thickness of the biofilm on a tag used in a reactor experiment was known, the regression line was used to estimate the amount of biofilm ( $\text{mg VSS}/\text{cm}^2$ ) on a tag. The amount of biofilm ( $\text{mg VSS}$ ) on each tag was calculated assuming that the surface areas of all the tags were the same.



**Figure 8.1** Volatile suspended solids content of sample biofilms versus biofilm thickness.

## 8.2 REACTOR EXPERIMENTS

The following table indicates the types of experiments that were carried out in the reactors. The results of each batch of experiments will be presented and discussed in turn.

In the experiments, approximately 17.3 mg or 1.73 mg of toluene and 9.7 mg of PCE were injected into the reactors. In a 1.8 litre reactor, this lead to approximately, 9.6 mg/L, or 0.96 mg/L of toluene and 5.3 mg/L of PCE. The three reactors were sampled and monitored for approximately 100 hours. The seven experiments carried out at the lower toluene concentrations were analyzed along with the rest of the toluene data by normalizing the concentration curves so that rate constants could be determined.

**Table 8.2 List of Experimental Scenarios**

Experiment #	Reactor contents	Toluene A	PCE B	Toluene & PCE C
1	De-ionized sterile water	-	-	*
2	Wastewater	*	-	*
3	Wastewater & tag	*	*	*
4	Wastewater & tag & scrapings from headworks	*	-	-
5	Sterile de- ionized water & tag & scrapings from headworks	*	-	-

\* Experiment completed

- Experiment not carried out due to time constraints

The wastewater used in all the experiments was taken from the raw influent into the Guelph wastewater treatment plant (GWWTP). The scrapings used in experiment 4 and 5 were taken from the walls of the headworks, in the same general area where the tags were suspended in the wastewater flow.

### 8.2.1 Results for experiment 1C

Figures 8.2 and 8.3 show the results from experiment 1C. In this experiment sterile, deionized water was spiked with both toluene and tetrachloroethylene (PCE). This experiment was a control. Figure 8.2 shows the variation in toluene concentration in all three reactors. Figure 8.3 shows the variation in the PCE concentration. The VOC concentration is displayed on the y axis and the time in hours on the x axis. Each data point on the graph is an average of a duplicate sample.

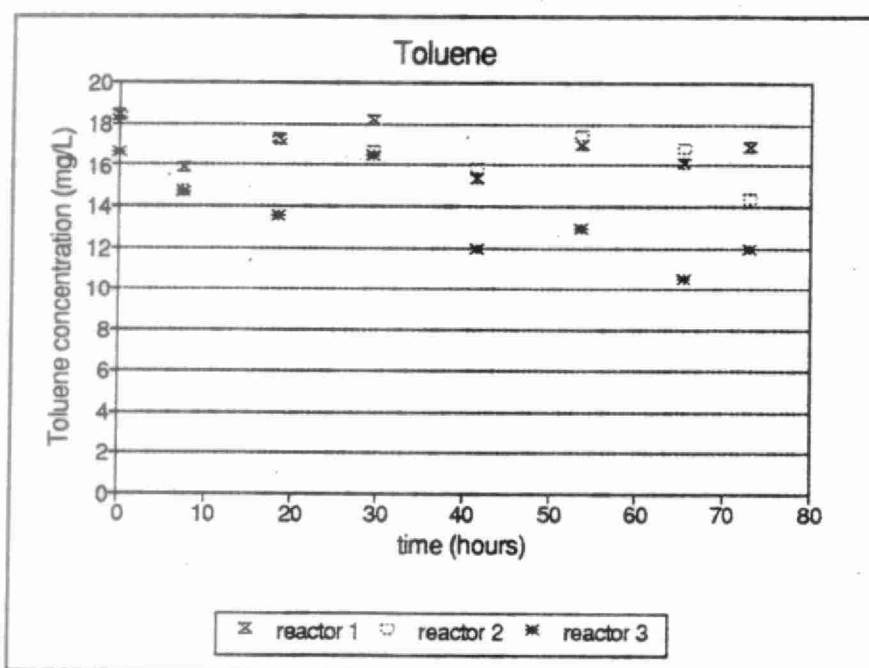
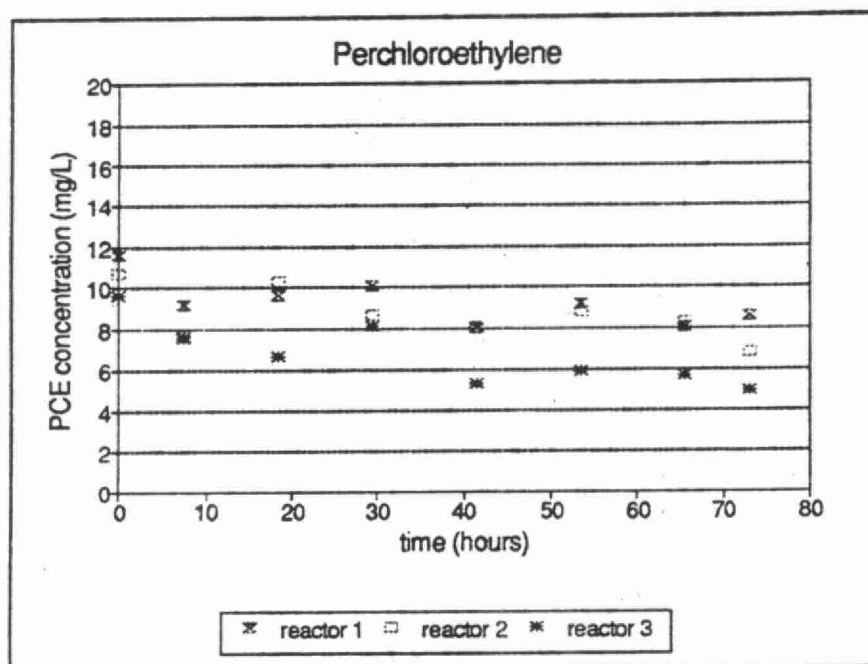


Figure 8.2. Variation in toluene concentration for reactors containing sterile water and spiked with a mix of toluene and PCE.

It appears that the largest loss of toluene occurred in reactor number 3. The concentration in reactor 3 was 13.3 mg/L with a standard deviation of  $\pm 2.8$  mg/L. The other reactors, 1 and 2 had average concentrations of  $16.9 \text{ mg/L} \pm 1.8 \text{ mg/L}$  and  $16.5 \pm 2.0 \text{ mg/L}$  of toluene respectively. The average concentration and the standard deviation for both toluene and PCE were calculated using all the concentration data gathered during the experimental run. This variability between the average concentration is lower in the PCE data.



**Figure 8.3.** Variation in the PCE concentration in reactors containing sterile water and spiked with toluene and PCE.

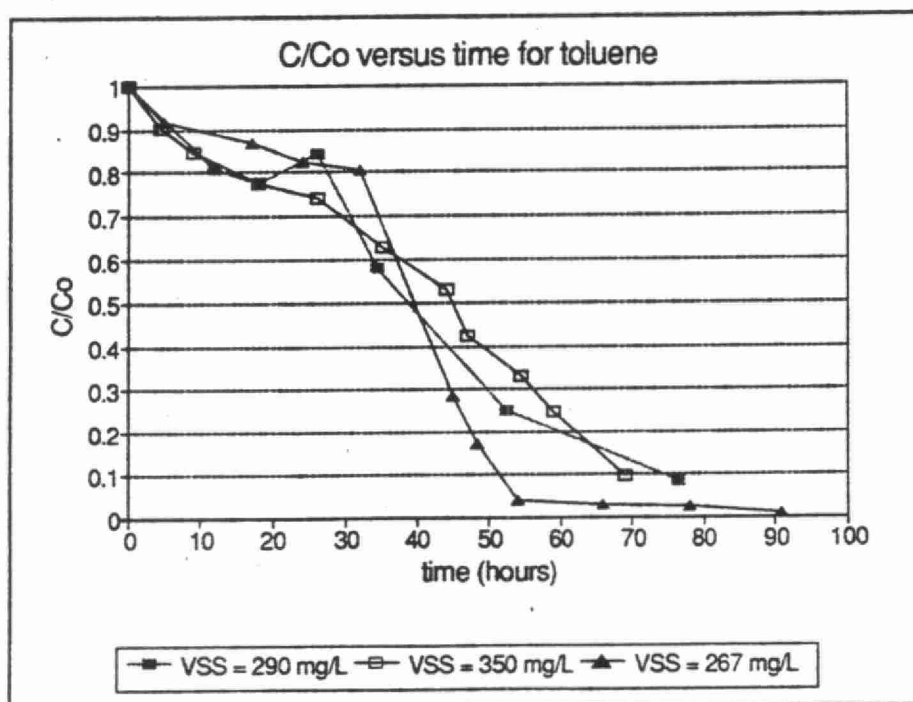
The average PCE concentrations in reactors 1, 2 and 3 were  $9.3 \pm 1.4 \text{ mg/L}$ ,  $8.7 \pm 1.4 \text{ mg/L}$  and  $6.7 \pm 1.8 \text{ mg/L}$  respectively. The PCE and toluene concentrations are higher than expected. The two contributing factors that would account for the higher than expected readings include: 1) an injection of VOC greater than 1 millilitre and 2) an error

in the VOC standards preparation. The needles used to inject the samples into the reactors were 20 gauge stainless steel, 6 inches long. This provided a small volume space for a small amount of extra VOC to be retained in the needle and then injected into the reactors. This volume was estimated to be close to 0.2 millilitres. This would adjust the amounts of toluene and PCE injected by an increased amount of only 20 %. The other contributing factor to the high readings was the possibility that despite shaking on a wrist-shaker and sonicating with heat for 15 minutes, the initial VOC mixture used to make the standards did not completely dissolve in the water. This would result in a calibration curve that would predict concentrations slightly higher than expected.

These experiments indicate that over an 80 hour time period; there is little loss of toluene or PCE from the reactors via sorption, loss into the 10 millilitre headspace or by mass transfer across the Gortex tubing.

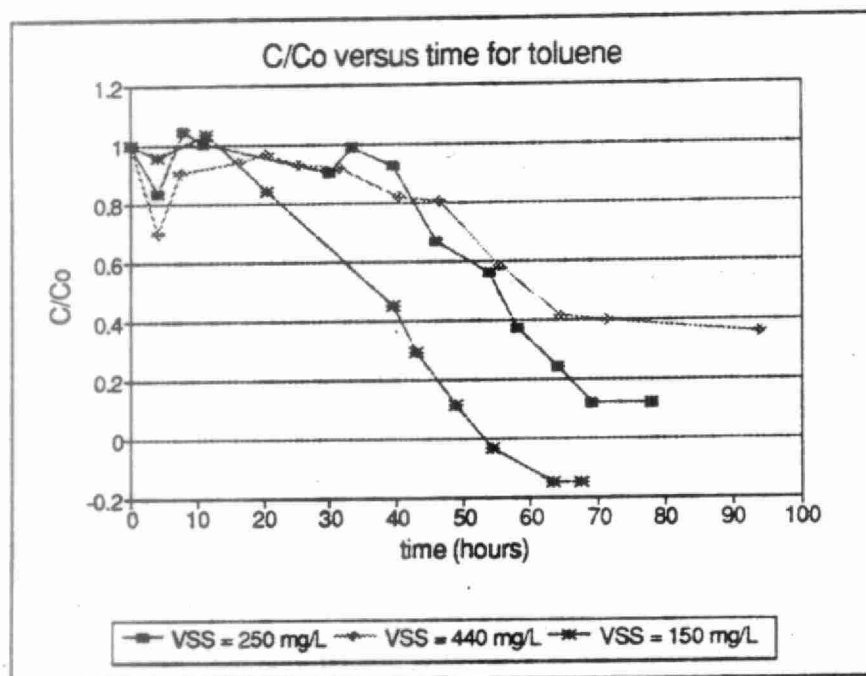
### 8.3 RESULTS OF EXPERIMENT 2A & 2C

Two types of VOC in wastewater experiments (Experiment 2A and 2C) were carried out. Experiment 2A consisted of wastewater injected with only toluene. The normalized graph of toluene concentration versus time for three experimental runs of this experiment is presented in Figure 8.4. The graph was normalized so that despite variability in the initial concentrations, the trends in the data could be easily observed. The VSS of the wastewater is also shown. The concentration of toluene in the wastewater appeared to decrease slowly and after 30 hours, a sharp decline in the concentration can be observed, for two of the experiments.



**Figure 8.4.** Normalized toluene concentration for experiment 2A, showing the biodegradation of toluene in the reactors.

In experiment 2C wastewater was injected with both toluene and PCE and the concentration of both chemicals was monitored.



**Figure 8.5.** Normalized toluene concentrations for experiment 2C, showing biodegradation of the toluene.

The concentration of toluene in the wastewater appears to remain constant for approximately 18-25 hours before any decrease in the toluene concentrations was observed, as shown in Figure 8.5. This could correspond to an acclimation period or a period of time during which the microbes consume the easily biodegradable organic matter in the wastewater before beginning to consume the toluene. From Figure 8.5 it appears that the higher the VSS of the wastewater the longer this "acclimation" period.



Figure 8.6 presents the PCE concentrations in reactors containing wastewater that were injected with both toluene and PCE. There did not appear to be an acclimation period for the microbes degrading PCE. There was a small decrease in the concentration of PCE and the initial amount of VSS available in the wastewater did not seem to affect the rate at which the PCE concentration decreased. This is expected as toluene would be preferentially metabolized since it is a nonchlorinated compound.

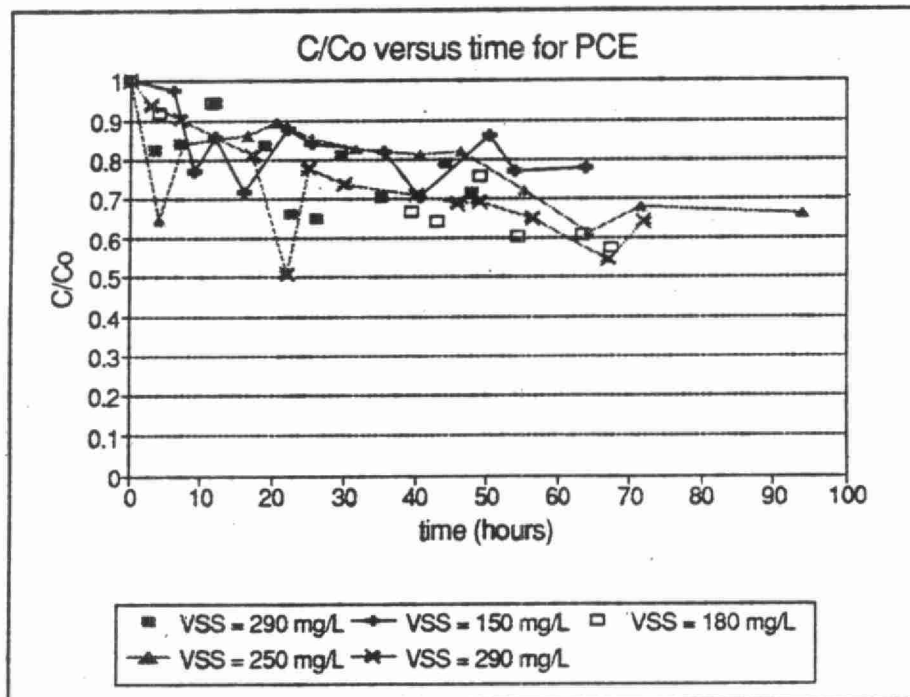
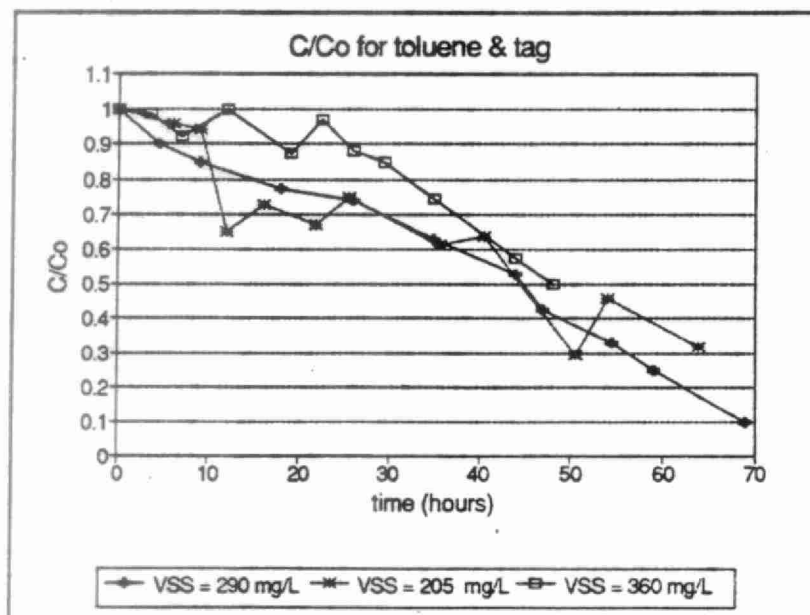


Figure 8.6. Normalized PCE concentration in experiment 3C.

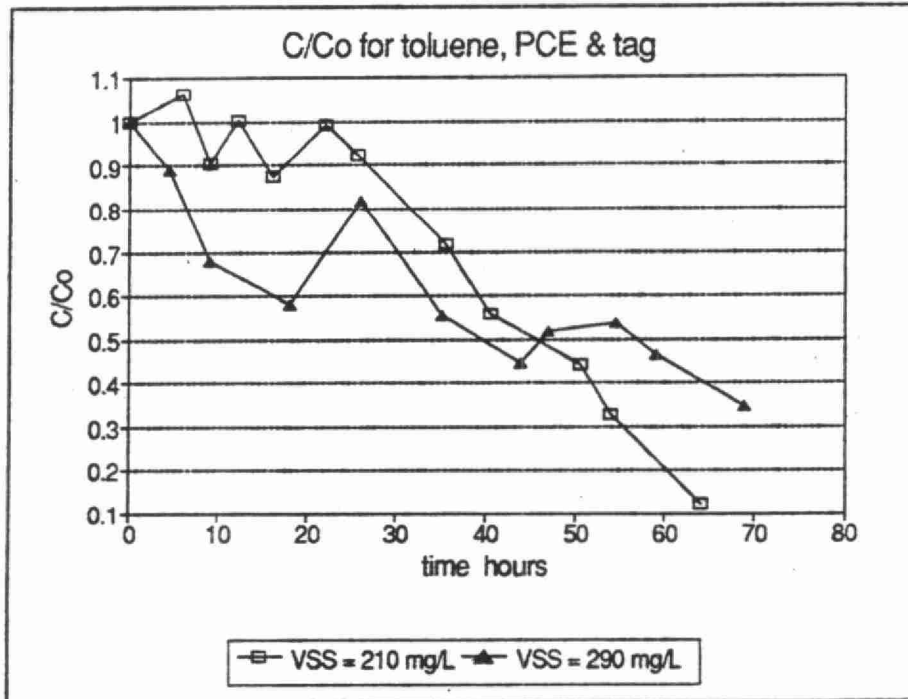
## 8.4 RESULTS OF EXPERIMENT 3A, 3B & 3C

In experiment 3 the reactors were filled with wastewater and biofilm coated tags. They were then injected with either toluene (experiment 3A ) or PCE (experiment 3B) or a mix of the two VOCs (experiment 3C) and the disappearance of the VOCs was observed. Figure 8.7 shows the normalized curves of toluene concentration versus time for experiment 3A for three of the seven experimental runs. The VSS presented is the total in the reactor. It includes the VSS of the biofilm and wastewater. There appears to be an acclimation period for the microbes that was as short as 12 hours in the reactor <sup>205 mg/L</sup> containing a VSS of ~~360~~ mg/L, 25 hours in the reactor with a VSS of <sup>360 mg/L</sup> ~~205~~ mg/L and there was no apparent acclimation period in the third reactor. The amount of VSS was larger in the reactor that had the longer acclimation period.



**Figure 8.7.** Normalized toluene concentrations for toluene & tag experiments.

The normalized curves showing the toluene concentration in the two experimental runs carried out for experiment 3C are displayed in Figure 8.8. The VSS represents the total in the reactor, it includes the VSS of the biofilm and wastewater.



**Figure 8.8.** Normalized toluene concentration for toluene, PCE & tag, experiment 3C.

In Figure 8.8, one experimental run shows an acclimation period of about 20 hours and the other does not show any acclimation period at all. During the 60-70 hour time period in Figure 8.7 the percent of toluene remaining in the reactors ranges from 10-30%, and in the case of the reactors contain PCE as well as toluene it ranges from 10-50%.

Figures 8.9 and 8.10 show the PCE concentrations for experiment 3B and 3C. In Figure 8.9 after about 50 hours, approximately 75-90 % of the PCE remained in the reactors. In contrast to this as displayed in Figure 8.10 at approximately 50 hours there was only 30-40% of the PCE remaining in the reactors that contained both toluene and a biofilm coated tag. It would appear that once toluene was in the water the biodegradation of PCE took place faster. Perhaps some metabolic pathways used by the microbes for the breakdown of toluene could also break down PCE.

In Figure 8.10, in all three reactors there did not appear to be an acclimation period as such, there is in general a relatively rapid decrease during the first 10 hours, then a 30-hour time period during which there is only a very slow decrease in the PCE concentration. At the end of this 30 hour period a slightly faster decrease was observed until less than 10% of the PCE remained.

It would also appear from Figures 8.9 and 8.10 that PCE was biodegraded at a faster rate than the toluene. In Figure 8.10, in the reactor containing a VSS of 210 mg/L during the first 20 hours the PCE concentration appears to decrease. The toluene concentration in this reactor (Fig 8.9) during this same time period remained fairly constant displaying an acclimation period. During the next 40 hours in this reactor there is a rapid decrease in the toluene concentration until less than 10 % remained, but the PCE concentration has remained relatively constant having only been reduced to 50 %

of the initial concentration. The microbes in the reactor appear to have alternated substrates, initially biodegrading the PCE and then turning to the toluene. This is rather unusual since toluene is generally considered to be simple to degrade, because it is not halogenated. It is possible that the fixed biomass (biofilm) attached to the tags and any large suspended clumps of biomass absorbed PCE and started to biodegrade it. The majority of the suspended biomass were consuming the more easily biodegradable organic matter in the wastewater and when that was consumed they turned to toluene. This would account for the fact that the PCE did not have an acclimation period, and it would be degraded anaerobically in the inner layers of the biofilm and the clumps of suspended biofilm.

In the reactor that had a VSS concentration of 290 mg/L (Fig 8.10) the concentration of both toluene and PCE decreased to 60% and 35% of the initial concentrations in the first 20 hrs. The PCE concentration then remained relatively constant for the next 30 hours, before decreasing slowly until less than 10 % remained. The toluene concentration also remained relatively constant for the next 50 hours till only 30 % of the initial concentration remained. The decrease in the VOCs in this reactor followed a similar pattern to each other and did not follow the trend observed in the reactor containing 210 mg/L of VSS.

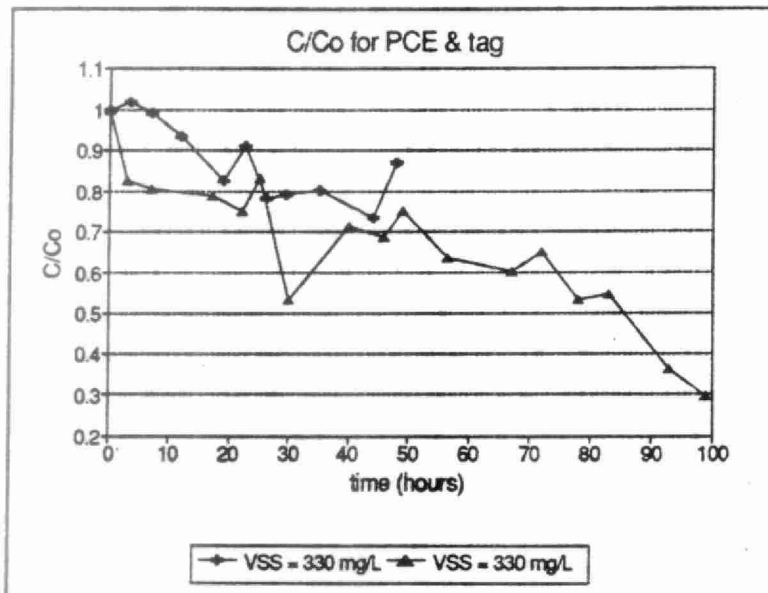


Figure 8.9. Normalized PCE concentration for PCE & tag, experiment 3B.

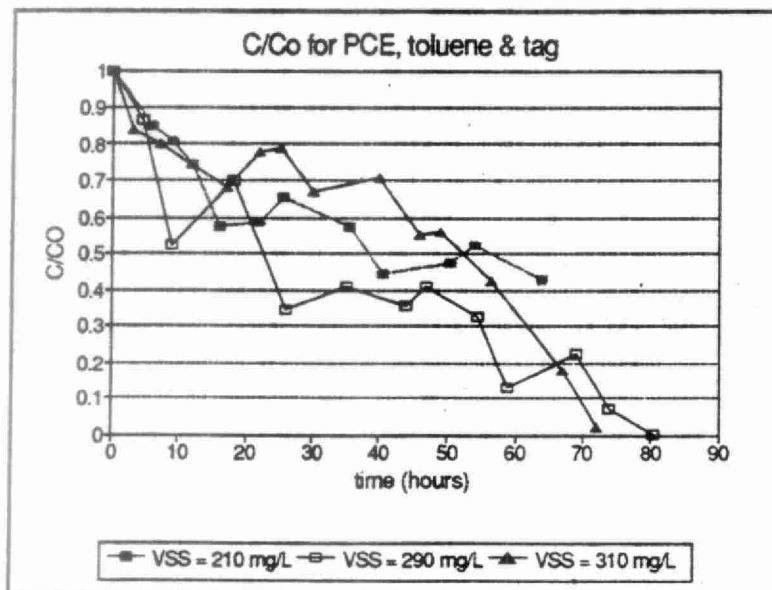
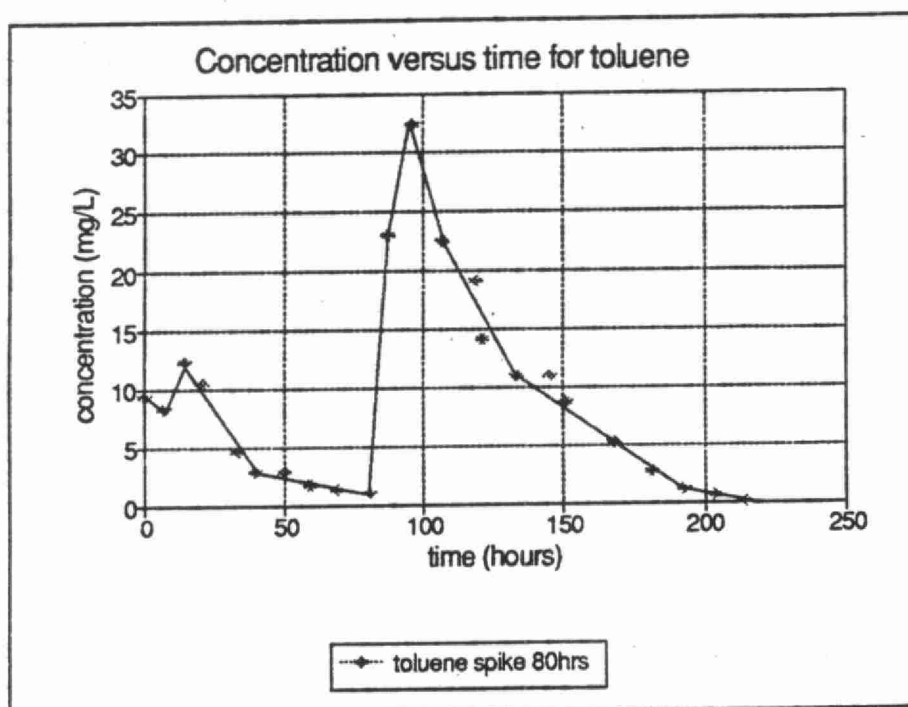


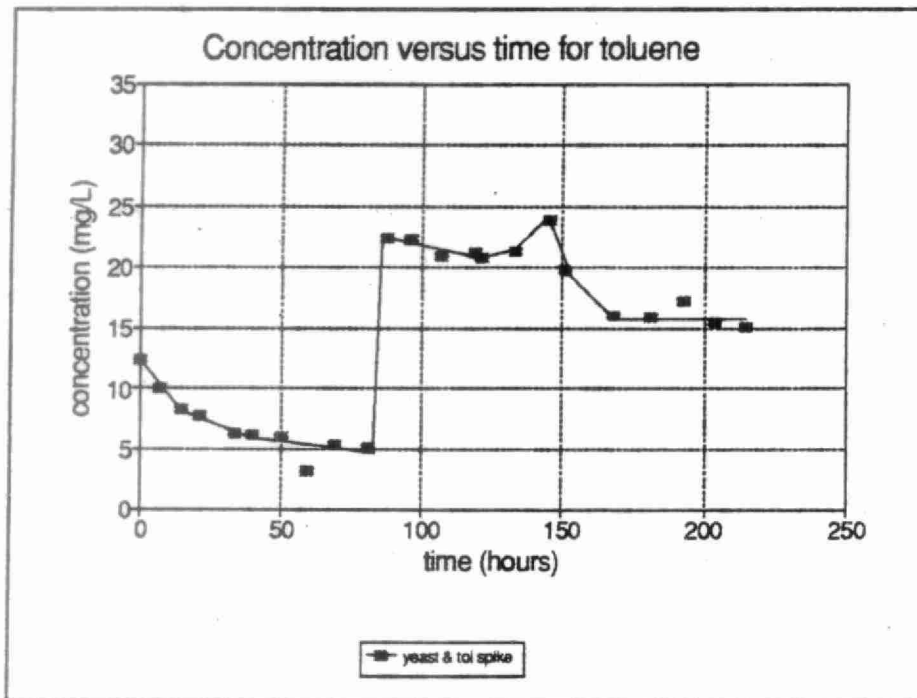
Figure 8.10. Normalized PCE concentration PCE, toluene & tag, experiment 3C.

Figure 8.11 is presented to demonstrate the fact that microbes are consuming toluene. The reactor contained toluene, wastewater and a biofilm-coated tag. Microbes consumed the toluene and when the reactor was spiked with 17.3 mg of toluene the microbes rapidly began to biodegrade the toluene again. There is a sharp increase in the toluene concentration as the toluene added had to slowly dissolve to into the wastewater. This was then followed by a rapid disappearance of toluene in the reactor.



**Figure 8.11.** Variation in the toluene concentration for a reactor biodegrading toluene and then spiked with toluene at approximately 80 hours.

Figure 8.12, corresponds to a reactor within which biodegradation of toluene occurred. The reactor was spiked at approximately 80 hours after the initial injection of toluene with 0.1 percent yeast extract and 17.3 mg of toluene. The amount of toluene in the reactor then remained almost constant for the next 100 hours. This was the only experiment of this type carried out. The data curve may suggest that the microbes preferentially degraded the more easily biodegradable available nutrients rather than toluene.

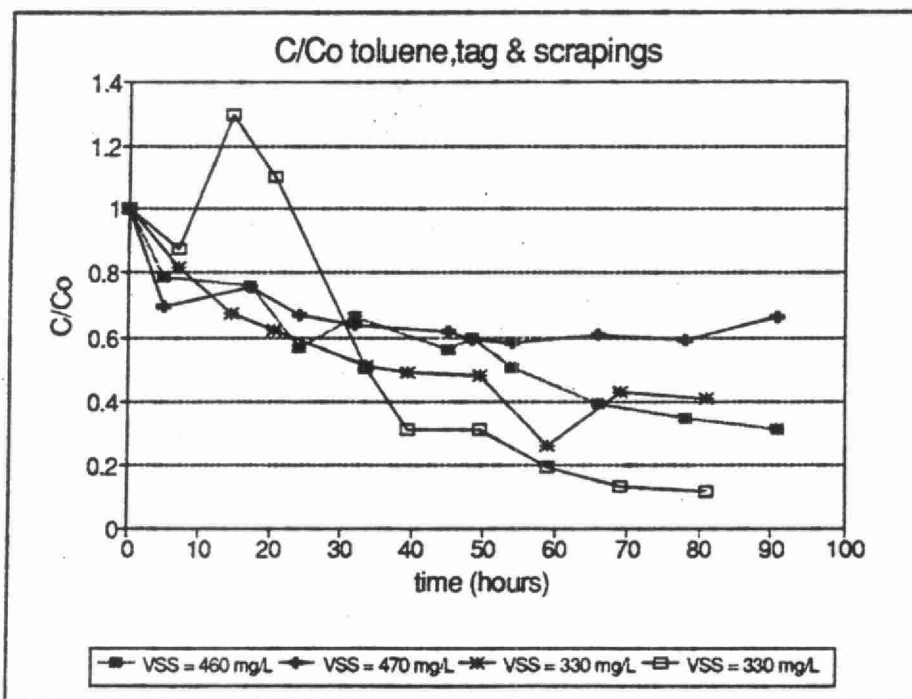


**Figure 8.12.** Variation in the toluene concentration for a reactor biodegrading toluene and spiked with toluene and a 0.1 % yeast extract solution at approximately 80 hours.



## 8.5 RESULTS FOR EXPERIMENT 4A

In this experiment the reactors were filled with wastewater, biofilm-coated tags and scrapings from the walls of the headworks at the GWWTP. The reactors were then injected with toluene and the disappearance of the VOC monitored. Figure 8.13 shows the normalized curves of the toluene concentration versus time for the results of the four experimental runs.



**Figure 8.13.** Normalized toluene concentrations for toluene, tag & scrapings (experiment 4A).

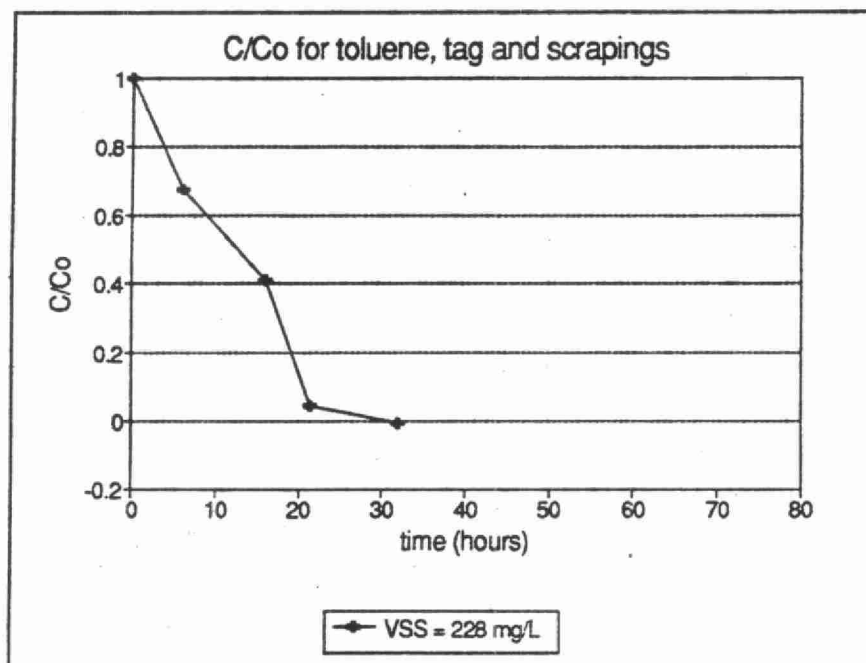
In only one experimental run was there a clearly visible time period after which toluene started to be removed from the reactors. At about 70 hours there was still 20-60% of the toluene remaining in the reactor. When the VSS in the reactor was around 400 mg/L the rate of toluene removal in the reactor was much less. The scrapings were taken from the walls of the entrance to the treatment plant in the same location where the tags were submerged. When this sample of VSS was added to the reactors, even though it provided more biomass, it also provided more organic matter for the microbes to consume.

The VSS concentration of the scrapings that were added to the reactors was high, approximately 920 mg/L in the reactors that contained 460 and 470 mg/L total VSS concentrations. For the other reactors that contained 330 mg/L total VSS the scrapings that were added had a VSS of 775 mg/L. The large amount of VSS placed in the reactors would increase the amount of BOD in the reactors and the microbes would biodegrade the more easily available nutrients and much less toluene would be removed from the reactors.

## **8.6 RESULTS OF EXPERIMENT 5A**

In this experiment the reactors were filled with deionized water, biofilm coated tags and scrapings from the headworks wall, and were then injected with toluene. Figure 8.14 shows the normalized curves of the toluene concentration versus time for the only experimental run.

In this case the VSS that was added to the reactor included the biofilm on the surface of the tag as well as scrapings. There was no time delay and the microbes consumed all of the toluene in the reactor in approximately 30 hours. The rapid removal of toluene is probably due to the fact that the microbes had no other source of nutrients except for the added scrapings. In this case the VSS concentration of the scrapings that was added to the reactor was only 116 mg/L. The total VSS concentration in the reactor was 228 mg/L and this includes 112 mg of VSS contributed by the biofilm on the tag.



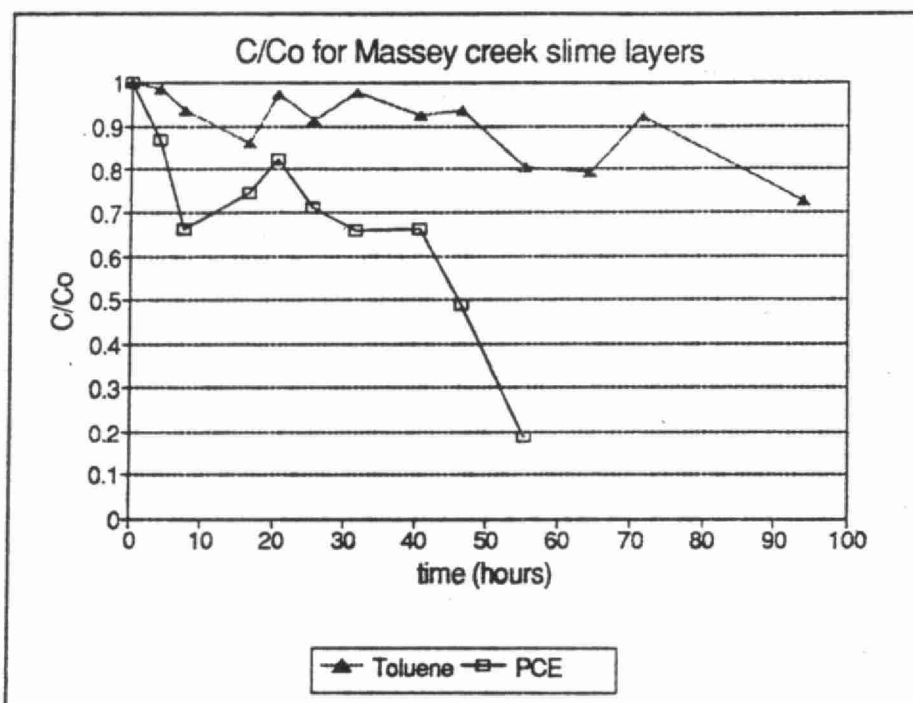
**Figure 8.14.** Normalized toluene concentrations for toluene, tag, sterile water and scrapings (experiment 5A).

## 8.7 MASSEY CREEK EXPERIMENTS

Figure 8.15 shows the results for the two experiments carried out using wastewater, slime layers and VOC. Fifty grams of slime taken from the walls of a heavily industrialized sewer line at Massey Creek were placed in the reactors.

The curve with the triangular data points shows the results of the toluene injection into the reactor and the second curve, the PCE concentrations for the injection of only PCE. After the slime was added to the reactors a sample of the wastewater in the reactor was analyzed before toluene was injected, and before the PCE was injected. The resulting gas chromatographs indicated that both toluene and PCE were present in the wastewater. This indicates that there was some background amount of these chemicals, however no attempt was made to quantify the amount. Over 100 other peaks were noted but no attempt was made to determine the quantities and types of other chemicals that were contaminating the slime.

In figure 8.15 after about 30 hours, the microbes began to biodegrade the PCE, however there was still 75 % of the toluene remaining at about 90 hours. The slime layers that were added to the reactor were clumped together. The dissolved oxygen concentrations of the wastewater in this reactor was in the range of 1 mg/L typical for a sewer. It is possible that anaerobic degradation was taking place inside the clumped slime-layer where the dissolved oxygen concentration would be even less than that of the wastewater.



**Figure 8.15.** Normalized VOC concentrations versus time using Massey Creek slime layers.

## 8.8 OVERVIEW

There occasionally was an acclimation period in the reactors that were biodegrading toluene. This acclimation period seem to last longer in reactors with higher concentrations of VSS. The reactors were permitted to biodegrade toluene and then spiked with toluene once the concentration has dropped to low levels and the rapid decrease of toluene was observed. This indicated that the microbes were now acclimated to the toluene. When 1 ml of a 0.1 % yeast extract was injected with the toluene, the toluene concentration in the reactor remained at high levels. This indicated that providing there is an alternative substrate that is easier to biodegrade, the microbes will not biodegrade the toluene. The lag time observed in the reactors before the microbes are acclimated to the VOCs, and the fact that WWTP receive relatively high levels of BOD suggest that the suspended biomass in sewer would not have time to become acclimated to or need to biodegrade any VOCs present.

## BIODEGRADATION RATE CONSTANT

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### 9.1 DETERMINATION OF BIODEGRADATION CONSTANT

The concentrations, times and VSS data for four sets of experiments were organized, and the files were imported into MathCAD spreadsheets to quantify biodegradation rate constants. MathCad was then used to carry out the regressions, both linear and non-linear to determine which model best fit the data. Several different models were tried. MathCad is a software program that has an error minimization routine, that will provide best fit parameters to an initial guess. The model that best fit the data visually and gave the smallest mean squared errors for the data was a first order differential equation:

$$\frac{dC}{dt} = K_{overall} C VSS \quad (12)$$

C = concentration of VOC in the reactor (mg/L)

t = time (h)

VSS = amount of VSS in the reactor (mg/L) at time, t = 0.

K<sub>overall</sub> = the overall biodegradation constant for the  
reactor (L/(mgVSS·h))

The analytical solution to this equation is:

$$\frac{C}{C_0} = e^{-K_{\text{overall}} \text{VSS} (t - t_0)} \quad (14)$$

where

$C_0$  = initial concentration of VOC in the reactor (mg/L)

$t_0$  = initial time (h)

The two parameters estimated by MathCad were  $K_{\text{overall}}$  and  $t_0$ . The toluene data had visible "acclimation periods". The graphs of all the toluene data were plotted and estimates of where this acclimation period ended were obtained using a ruler and considered to be a new initial time. Following this, the decay in the VOC was fitted by removing the lag phase segment of the data set, which was then entered into Mathcad. This  $t_0$  ranged from 10 to 40 hours.



## 9.2 RESULTS OF THE NON-LINEAR REGRESSION

The overall biodegradation rate constants and the initial time for the four main experiments are presented in Table 9.1. The mean square error of the fit is also presented.

**Table 9.1 Biodegradation rate constants determined from Mathcad**

Experiment	$K_{\text{overall}}$ L/mg VSS. hr	$t_0$ hours	Mean Squared Error
Toluene & wastewater only [3 data sets]	$1.2 \times 10^{-4}$	16	0.02
Toluene & wastewater & PCE [7 data sets]	$8.9 \times 10^{-5}$	20	0.08
Toluene & wastewater (the two data sets above combined) [10 data sets]	$8.8 \times 10^{-5}$	19	0.07
Toluene & wastewater & biofilm [4 data sets]	$6.7 \times 10^{-5}$	22	0.03
PCE & wastewater & toluene [6 data sets]	$1.8 \times 10^{-5}$	-11.0	0.01
PCE wastewater & biofilm [2 data sets]	$2.9 \times 10^{-5}$	-0.93	0.01

The biodegradation constant for toluene in the reactor with wastewater was the largest; it was an order of magnitude larger than all of the other biodegradation rate constants. The biodegradation constants for reactors which contained both toluene and PCE were only slightly smaller.

The time delay that describes the acclimation period is  $t_0$ . Most of the PCE data did not have acclimation periods as a result the  $t_0$  predicted by the model was negative. The negative result was simply due to the least squares fit through the data.

Figure 9.1 and 9.2 shows the predicted versus the measured data for toluene, wastewater and biofilm.

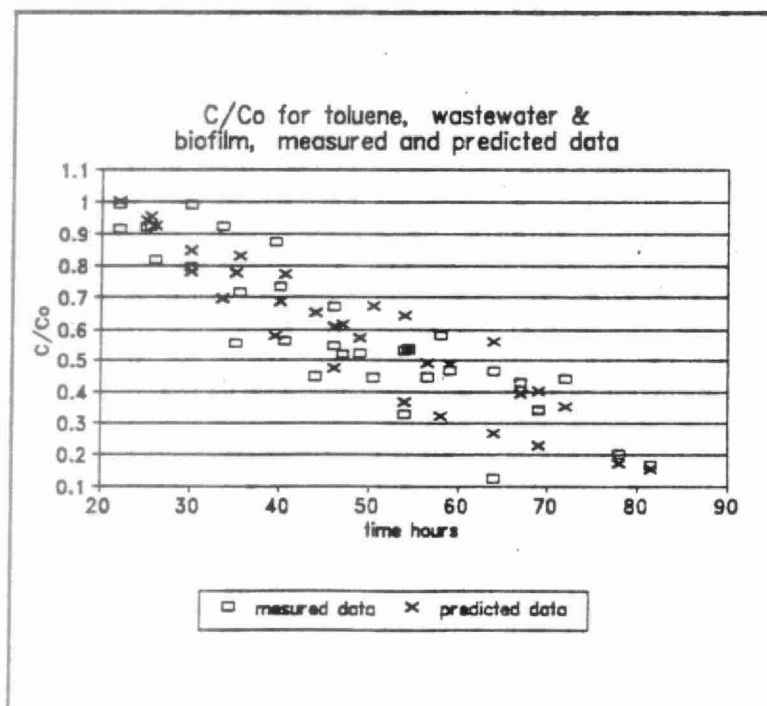
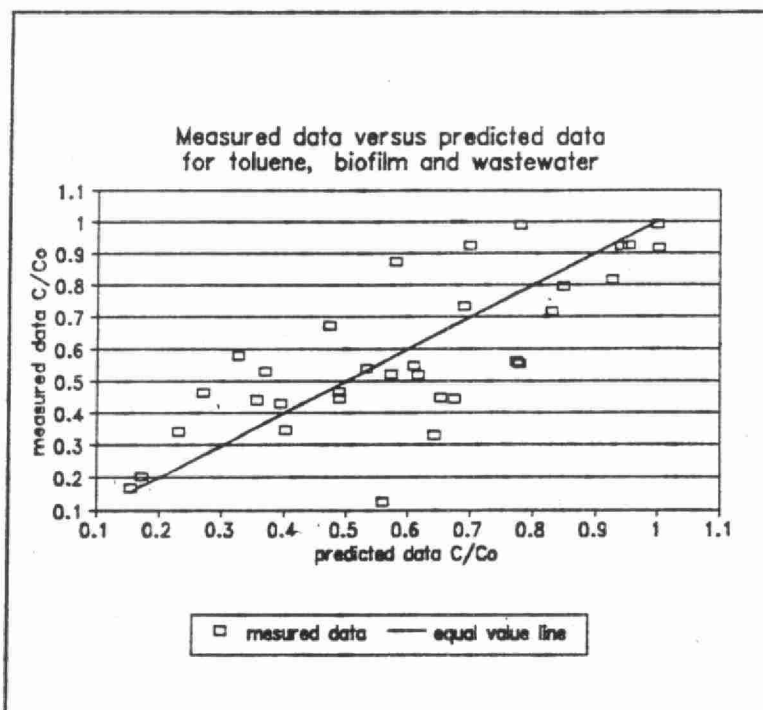


Figure 9.1. Plot of the measured data and the predicted data versus time



**Figure 9.2.** Plot of the measured versus the predicted data for toluene, wastewater and biofilm

The PCE biodegradation rate constant was of the same order of magnitude as for toluene. This seems to be rather unusual since toluene is generally considered to be an easily biodegradable compound while PCE is a recalcitrant. A biodegradation rate constant found in the literature of  $3.54 \times 10^{-4} \text{ L}/(\text{mg MLVSS} \cdot \text{h})$  (Bell *et al.*, 1989) for tetrachloroethylene is larger than the ones presented in Table 9.1 by an order of magnitude. The value determined by (Bell *et al.*, 1989) was obtained for activated sludge, in a pilot plant experiment where the biodegradation was not measured directly but assumed from a mass balance difference.

A biological rate constant for the biodegradation of toluene of  $0.016 \text{ L}/(\text{mg MLVSS} \cdot \text{h})$  was taken from Namkung and Rittman (1987). They obtained this rate constant from a lab scale activated sludge treatment system. This value used in chapter six, is 100 times larger than the biodegradation rate constant for toluene determined in the reactor experiments. Use of the biological rate constant determined by Namkung and Rittman would greatly overestimate the amount of biodegradation taking place in the sewer. Activated sludge contains a larger proportion of viable biomass than would the wastewater. Thus we can expect that the activated sludge should degrade much more VOC per mg of VSS than the wastewater.

### **9.3 NEW MODEL FOR BIODEGRADATION ALONG A SEWER LINE**

The biodegradation constant used in the new model was the one determined for toluene, wastewater and a biofilm coated tag. This constant is an overall biodegradation constant that includes the biodegradation constant of the biofilm and the free suspended biomass in the reactor and the associated wastewater to biofilm mass transfer coefficients for this reactor.

The following equation is the biodegradation model that was developed to include the slime layer in the sewer, and free suspended biomass.

$$R_{bio} = -K_{overall} C ( X_a V_a + X_f A L_f ) \quad (15)$$

where

$K_{overall}$  = biodegradation rate constant ( $m^3/(g \text{ VSS} \cdot s)$ )

$V_a$  = the volume of liquid in the sewer ( $m^3$ )

$X_a$  = viable suspended biomass in sewers ( $g \text{ MLVSS} / m^3$ )

$X_f$  = density of the slime layer ( $g \text{ VSS} / m^3$ )

$A$  = wetted surface area ( $m^2$ )

$L_f$  = thickness of slime layer ( $m$ )

$C$  = concentration of VOC in the wastewater ( $mg/m^3$ )

There are several things that occur in a real sewers, that were not addressed in this model. For example the time lag that took place in the reactors, during which suspended microbes consume easily biodegradable material in the reactors, before biodegradation of the VOC begins to occur. The residence time of wastewater in sewers is generally much shorter than this time lag, therefore the microbes may not have a chance to act on the VOCs.

The mass transfer coefficients incorporated in the overall biodegradation rate constant are for the batch reactors used to carry out these experiments. The mass transfer coefficients for the sewer would be highly variable, depending on flow conditions. This model simplifies the biodegradation process in the sewer however it is a big improvement on existing knowledge.

The amount of viable biomass in the sewers ( $X_a$ ) was estimated by the author in terms of MLVSS for use with activated sludge biodegradation rate constants. It should be noted that the value of  $X_a$  used in this model was 100 mg VSS/L. This was the largest amount of viable biomass estimated in the literature review. A conservative estimate of the effects of biodegradation in the sewer can be ascertained by the use of the largest possible measurement for viable biomass.

#### 9.4 RESULTS OF MODEL ANALYSIS

The same set of conditions found in Table 6.1 was used, except that a new biodegradation rate constant of  $1.8 \times 10^{-8}$  ( $\text{m}^3/(\text{g VSS} \cdot \text{s})$ ) was applied. The magnitude of  $X_a$  chosen was 100 g VSS/ $\text{m}^3$ .

Figure 9.3 is a graph showing the results displayed in Table 9.3 (removal of toluene along a 5-km reach). It was predicted that practically no biodegradation would take place and that all of the removal of toluene would be due to stripping.

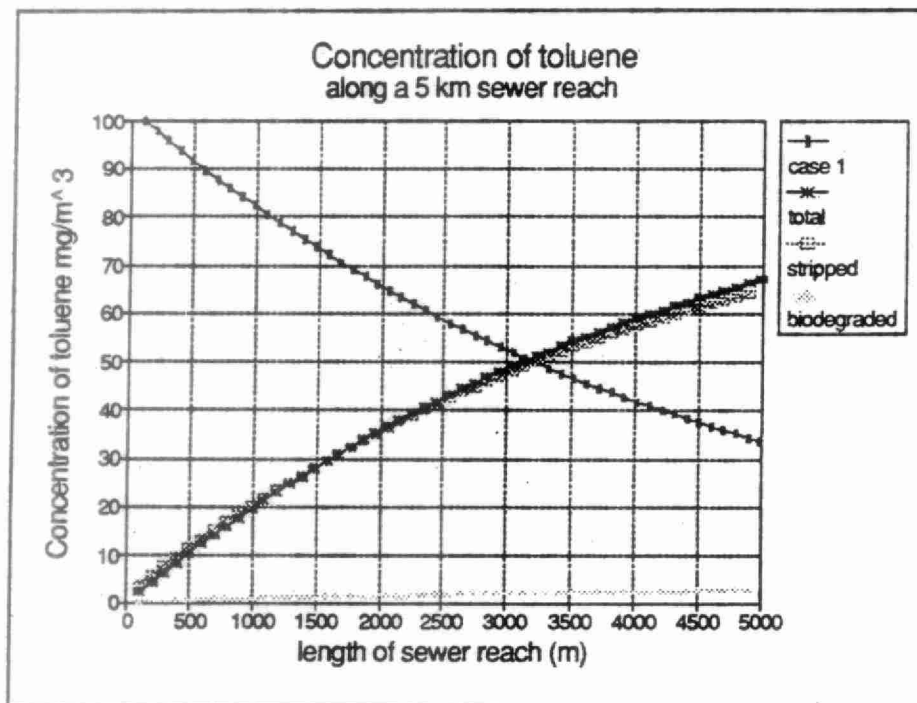
**Table 9.3 Model analysis**

	Case 1
Vent rate (m <sup>3</sup> /s)	0.11
$X_a$ (g VSS/m <sup>3</sup> )	100
$K_{la}$ (1/hr)	0.7452
Depth (m)	0.15
Removal %	65
% stripped	99
% biodegraded	1

Therefore, using the experimental biodegradation constant the amount of toluene removed by biodegradation is quite small even when a large value of the suspended biomass concerned is used. The problem associated with using the reactor biodegradation constant to generalize the conditions in a sewer lies with the mass

transfer coefficients that are hidden in the overall biodegradation constant.

The mass transfer conditions in the reactor were not addressed and are possibly not very similar to those in a sewer.



**Figure 9.3.** Model prediction of the toluene concentration along a sewer reach.



## CONCLUSIONS

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1. The proportion of volatile suspended solids in sewers that is viable biomass is very small.
2. In sewers, toluene and PCE would be degraded only after substantial degradation of available organic matter. The microbes in the reactors biodegraded the toluene after a lag phase. This lag phase was likely caused by the presence of easily biodegradable organic matter that the microbes consume and when this is all gone the microbes turn their attention to the toluene or PCE. The time lag in the reactors suggests that in a sewer, as long as there is organic matter to consume, the microbes will not biodegrade the VOCs.
3. Four biodegradation rate constants were determined from reactor experiments. These biodegradation rate constants for toluene and PCE by suspended and fixed biomass are much smaller than reported values for acclimated activated sludge systems.
4. Model predictions indicate that biodegradation is likely very small relative to volatilization in sewers.

## FURTHER STUDY

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1. Attempts should continue to estimate biodegradation rate constants for the slime layer itself. Unlike the suspended biomass where the biomass has a certain amount of time to act on the VOCs along a sewer reach, the biofilm can absorb the toluene and possibly biodegrade it at a later time. This could best be assessed by dynamic experiments carried out in a CSTR.

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## **Appendix A: Suspended Biomass Data**



Experiment: 1 Analysis of Raw composite wastewater & Activated sludge  
February 11th, 1993

A RAW DATA

Headworks wastewater

Collected at GWWTP 8:30 a.m.  
Dissolved oxygen concentration 7.52 mg/L  
Atmospheric pressure 736 mm Hg  
wastewater temp 12°C  
pH 8.4

Industrial wastewater

Collected at Silvercreek parkway 8:50 a.m.  
Dissolved oxygen concentration 4.2 mg/L  
Atmospheric pressure 736 mm Hg  
wastewater temp 9°C  
pH 8.25

Residential wastewater

Collected at Burns Drive 9:25 a.m.  
Dissolved oxygen concentration 4.9 mg/L  
Atmospheric pressure 736 mm Hg  
wastewater temp 10°C  
pH 8.35

Activated sludge

Collected at GWWTP 8:50 a.m.  
Dissolved oxygen concentration 4.9 mg/L  
Atmospheric pressure 736 mm Hg  
wastewater temp 9°C  
pH 8.03

B: CHEMICAL OXYGEN DEMAND ANALYSIS

Calibration Curve

Sample	Absorbance	Best fit	Regression Output:	
µg/ml	at			
	600nm		Constant	0.041042
62.5	0.025	0.053712	Std Err of Y Est	0.041004
125	0.04	0.066383	R Squared	0.825672
250	0.14	0.091724	No. of Observations	5
500	0.17	0.142407	Degrees of Freedom	3
1000	0.223	0.243773	X Coefficient(s)	0.000203
			Std Err of Coef.	5.38E-05

Sample	Absorbance	Absorbance	COD
		AVG	mg/L
HW1	0.108	0.1	290.8203
HW1	0.092		
HW2	0.117	0.113	354.9446
HW2	0.109		
RES1	0.078	0.091	246.4265
RES1	0.104		
RES2	0.141	0.150	534.9859
RES2	0.158		
IN1	0.074	0.071	145.3074
IN1	0.067		
IN2	0.053	0.0575	81.18304
IN2	0.062		

Experiment: 1 Analysis of Raw composite wastewater & Activated sludge  
February 11th, 1993

C: ATP ANALYSIS

Calibration Curve

Relative intensity versus ATP concentration

Standrad	Mole/ml	µg/L	Log		
s1	3.84E-08	19200	4.283301	Regression Output: Constant 1.039449 Std Err of Y Est 0.530034 R Squared 0.855491 No. of Observations 7 Degrees of Freedom 5	
s2	3.84E-09	1920	3.283301		
s3	3.84E-10	192	2.283301		
s4	3.84E-11	19.2	1.283301		
s5	3.84E-12	1.92	0.283301		
s6	3.84E-13	0.192	-0.7167	X Coefficient(s) 0.544967 Std Err of Coef. 0.100167	
s7	3.84E-14	0.0192	-1.7167		
s8	3.84E-15	0.00192	-2.7167		
s9	3.84E-16	0.000192	-3.7167		

	RI	RI	log(RI)	BEST FIT
s2	2000	1999.95	3.301019	2.82874
s3	350	349.95	2.544006	2.283773
s4	25	24.95	1.397071	1.738806
s5	3	2.95	0.469822	1.193839
s6	2.15	2.1	0.322219	0.648872
s7	1.5	1.45	0.161368	0.103905

Sterile water 0.05

Tris 0.05

D: ATP ANALYSIS

Light output from wastewater or sludge

Grab sample	Sample #	Realative intensity
INDUS	1	0.8
INDUS	2	0.65
INDUS	3	0.85
RES	1	3
RES	2	1.55
RES	3	1.6
HEAD	1	33
HEAD	2	35
HEAD	3	35.5
HEAD	4	27
AS	1	30
AS	2	32
AS	3	45

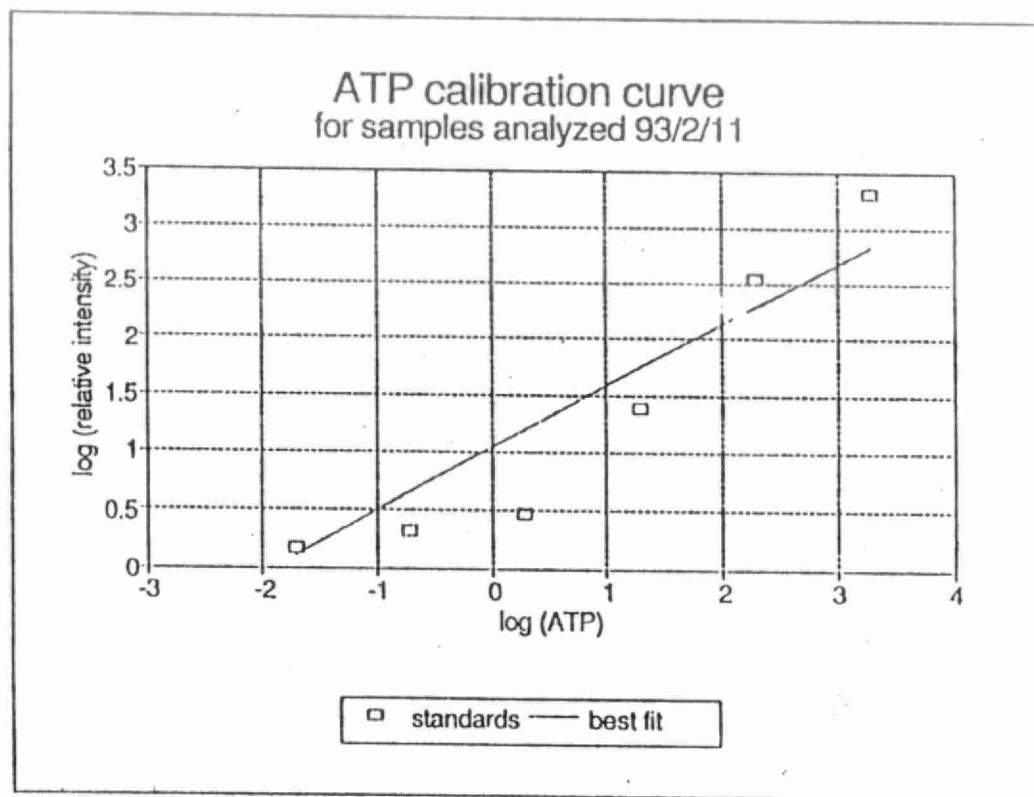
Experiment: 1 Analysis of Raw composite wastewater & Activated sludge  
February 11th, 1993

E: ATP ANALYSIS

	Log(S)	Log(ATP)	ATP µg/ml	Average µg/L	Xbio mg/L
INDUS	-0.09691	-5.08519	8.22E-06	7.67E-06	0.024054
INDUS	-0.18709	-5.25066	5.61E-06		
INDUS	-0.07058	-5.03688	9.19E-06		
			STD	1.85E-06	
RES	0.477121	-4.03186	9.29E-05	5E-05	0.156669
RES	0.190332	-4.55811	2.77E-05		
RES	0.20412	-4.53281	2.93E-05		
			STD	3.7E-05	
HEAD	1.518514	-2.12093	0.00757	0.007474	23.42852
HEAD	1.544068	-2.07404	0.008433		
HEAD	1.550228	-2.06273	0.008655		
HEAD	1.431364	-2.28085	0.005238		
			STD	0.0016	
AS	1.477121	-2.19688	0.006355	0.896077	
AS	1.50515	-2.14545	0.007154		
AS	1.653213	-1.87376	0.013373		
			STD	0.005	

Experiment: 1 Analysis of Raw composite wastewater & Activated sludge  
February 11th, 1993

F: ATP Calibration curve  
Relative intensity versus ATP concentration



Experiment: 1 Analysis of Raw composite wastewater & Activated sludge  
February 11th, 1993

HEADWORKS WASTEWATER

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L	mg/L	
1	1.1059	1.1112	106	1.1059	106	0.9933		2810	
2	1.1062	1.1134	144	1.1061	146	0.9935		2815	
3	1.105	1.1159	218	1.1109	100	0.9975		2835	
4	1.1043	1.111	134	1.1043	134	0.9902		2852.5	
5	1.1165	1.1236	142	1.1167	138	1.0035		2830	
6	1.1064	1.1157	186	1.11065	101	0.9934		2931.25	
AVG			155		120.83			2845.63	
STD			36.66		18.92			40.71	

INDUSTRIAL SEWER

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L	mg/L	
1	1.1132	1.1199	67	1.1139	60	1.0026		2782.5	
2	1.1166	1.1243	77	1.1166	77	1.0034		2830	
3	1.0981	1.106	79	1.0982	78	0.9858		2810	
4	1.1042	1.1097	55	1.1044	53	0.9905		2847.5	
5	1.1019	1.1096	77	1.102	76	0.9901		2797.5	
6	1.1022	1.1098	76	1.1022	76	0.98971		2812.25	
AVG			71.83		70.00			2813.29	
STD			8.45		9.78			21.05	

Experiment: 1 Analysis of Raw composite wastewater & Activated sludge  
February 11th, 1993

RESIDENTIAL WASTEWATER

Sample			TSS		VSS		FS
	g	g	mg/L	g	mg/L	g	mg/L
1	1.1135	1.1187	104	1.114	94	1.0021	2238
2	1.1123	1.1196	146	1.1113	166	0.9976	2274
3	1.1225	1.1282	114	1.123	104	1.0089	2282
4	1.1192	1.1249	114	1.1194	110	1.0052	2284
5	1.1142	1.1192	100	1.1143	98	1.0011	2264
6	1.1174	1.1227	106	1.1172	110	1.0029	2286
AVG			114		136.62		2271.333
STD			15.19		24.12		16.63998

ACTIVATED SLUDGE

Sample			TSS		VSS		FS
	g	g	mg/L	g	mg/L	g	mg/L
1	1.1100	1.1389	2890	1.1172	2170	1.0013	11590
2	1.1084	1.1373	2890	1.1158	2150	0.9990	11680
3	1.1069	1.1352	2830	1.1134	2180	0.9974	11600
4	1.107	1.1366	2960	1.1144	2220	0.9984	11600
5	1.1075	1.1374	2990	1.1146	2280	0.9983	11630
6	1.1062	1.138	3180	1.1134	2460	0.9958	11760
AVG			2956.67		2243.33		11643.33
STD			112.50		10.56		60.18

Experiment: 2 Analysis of Raw composite wastewater & Activated sludge  
February 18th, 1993.

A: RAW DATA

Headworks wastewater

Collected at GWWTP 8:30 a.m.  
Dissolved oxygen concentration 7.8 mg/L  
Atmospheric pressure 736 mm Hg  
wastewater temp 12.1°C  
Air temperature 15.5°C  
pH 8.46

Activated sudge

Collected at GWWTP 8:50 a.m.  
Dissolved oxygen concentration 4.9 mg/L  
Atmospheric pressure 736 mm Hg  
wastewater temp 9°C  
Air temperature 12.5°C  
pH 8.03

B: CHEMICAL OXYGEN DEMAND ANALYSIS

Calibration Curve

Sample µg/ml	Absorbance at 600nm	Best Fit	Regression Output: Constant	
62.5	0.025	0.053712	Std Err of Y Est	0.041004
125	0.04	0.066383	R Squared	0.825672
250	0.14	0.091724	No. of Observations	5
500	0.17	0.142407	Degrees of Freedom	3
1000	0.223	0.243773	X Coefficient(s)	0.000203
			Std Err of Coef.	5.38E-05

Sample	Absorbance	AVG	COD mg/L
HW1	0.091	0.1	290.8203
HW1	0.109		
HW2	0.166	0.1725	648.4367
HW2	0.179		
AS1	0.540	0.492	2224.415
AS1	0.444		
AS2	0.57	0.575	2633.824
AS2	0.58		

Experiment: 2 Analysis of Raw composite wastewater & Activated sludge  
February 18th, 1993.

C: ATP ANALYSIS

Light output from standrads

Calibration Curve

Standrads	Mole/ml	µg/ml	Log
s1	3.84E-08	19.2	1.283301
s2	3.84E-09	1.92	0.283301
s3	3.84E-10	0.192	-0.7167
s4	3.84E-11	0.0192	-1.7167
s5	3.84E-12	0.00192	-2.7167
s6	3.84E-13	0.000192	-3.7167
s7	3.84E-14	1.92E-05	-4.7167
s8	3.84E-15	1.92E-06	-5.7167
s9	3.84E-16	1.92E-07	-6.7167

Regression Output:  
Constant 2.429821  
Std Err of Y Est 0.387762  
R Squared 0.915048  
No. of Observations 5  
Degrees of Freedom 3  
  
X Coefficient(s) 0.697044  
Std Err of Coef. 0.122621

Standrads	RI	RI	log(RI)
s2	700	699.95	2.845067
s3	105	104.95	2.020982
s6	5.85	5.8	0.763428
s7	2.2	2.15	0.332438
s8	1.65	1.6	0.20412
Sterile water	0.05		
Tris buffer	0.05		

D: ATP ANALYSIS

Light out put from the wastewater and the  
activated sludge

Grab	Sample	Relative intensity
HEAD1	1	14.5
HEAD2	2	18.5
HEAD3	3	21.5
SLUDGE	1	15.5
SLUDGE	2	38
SLUDGE	3	23



Experiment: 2 Analysis of Raw composite wastewater & Activated sludge  
February 18th, 1993.

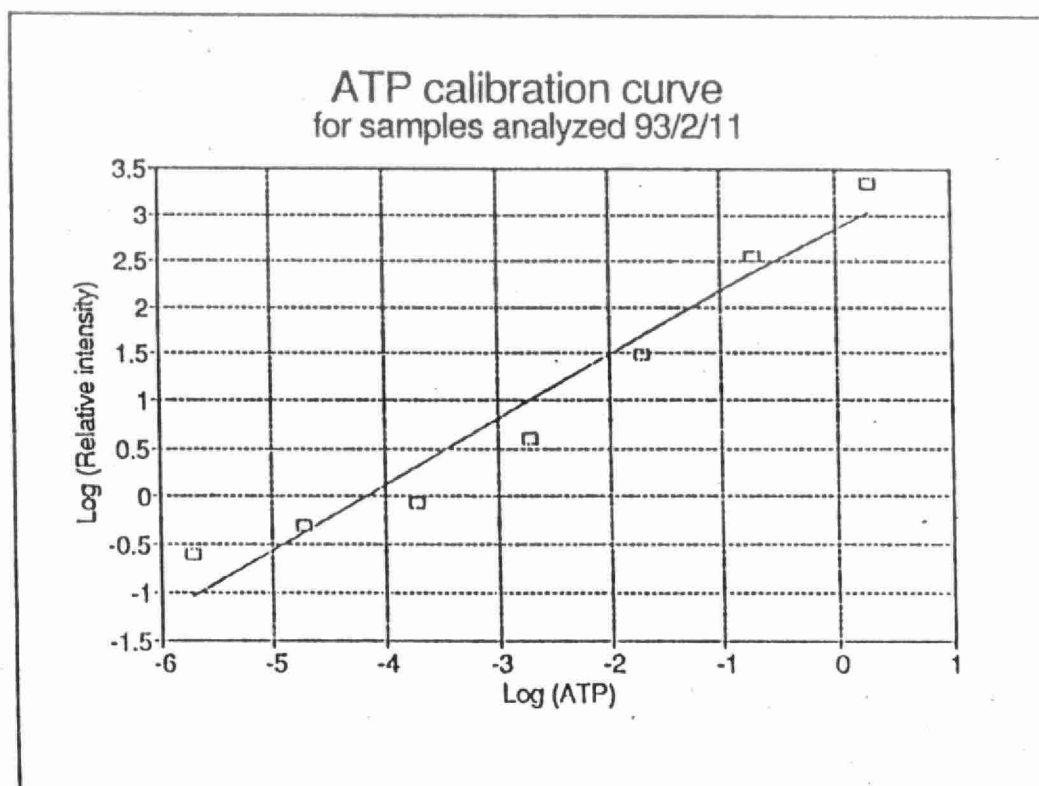
E: ATP ANALYSIS

Sample	Log(S)	Log(ATP)	ATP µg/ml	Average µg/ml	Xbio mg/L
HEAD1	1.161368	-1.81976	0.015144	0.02109	12.5893
HEAD2	1.267172	-1.66797	0.02148		
HEAD3	1.332438	-1.57434	0.026648		
			STD	0.0057	
AS	1.190332	-1.77821	0.016664	3.544871	
AS	1.579784	-1.21949	0.060327		
AS	1.361728	-1.53232	0.029355		
			STD	0.022	

Experiment: 2 Analysis of Raw composite wastewater & Activated sludge  
February 18th, 1993.

II: Calibration curve

Relative intensity versus ATP concentration



Experiment: 2 Analysis of Raw composite wastewater & Activated sludge  
February 18th, 1993.

G: TSS, VSS & FIXED SOLIDS ANALYSIS OF WASTEWATER

HEADWORKS WASTEWATER

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L		mg/L
1	1.1042	1.1257	215	1.1059	181	0.9935	2810		
2	1.1046	1.1236	190	1.1061	152	0.9935	2815		
3	1.1093	1.1235	142	1.1109	116	0.9975	2835		
4	1.101	1.1216	206	1.1043	171	0.9902	2852		
5	1.1145	1.1234	89	1.1167	80	1.0035	2830		
6	1.1048	1.126	212	1.11065	178	0.9934	2931		
AVG			175.6		146.33		2849		
STD			45.9		36.89		22.1		

ACTIVATED SLUDGE

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L		mg/L
1	1.1111	1.1348	2370	1.1168	1800	1.0007	2902.5		
2	1.1085	1.1336	2510	1.1142	1940	0.998	2905		
3	1.1085	1.1324	2390	1.1139	1850	0.9972	2917.5		
4	1.1092	1.1403	3110	1.1161	2420	0.9983	2945		
5	1.1094	1.1396	3020	1.1161	2350	0.9982	2947.5		
6	1.1068	1.137	3020	1.1136	2340	0.9958	2945		
AVG			2736.67		2116.67		2927		
STD			317.78		257.85		19.3		

# Experiment: 3 Analysis of Residential, Industrial & Raw-composite wastewater & Activated sludge March 2nd, 1993

## A: RAW DATA

### Headworks wastewater

Collected at GWWTP 8.10 a.m.  
 Dissolved oxygen concentration 6.2 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 12.1°C  
 pH 7.05

### Industrial wastewater

Collected at Silvercreek parkway 9:30 a.m.  
 Dissolved oxygen concentration 6.39 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 11.5°C  
 pH 6.39

### Residential wastewater

Collected at Burns Drive 9:55 a.m.  
 Dissolved oxygen concentration 6.2 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 10.3°C  
 pH 8.78

### Activated sludge

Collected at GWWTP 8.35am  
 Dissolved oxygen concentration 4.39 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 10°C  
 pH 7.05

## B: CHEMICAL OXYGEN DEMAND ANALYSIS

### Calibration Curve

Sample ug/ml	Absorbance at 600nm	Best fit
62.5	0.004	0.010409
125	0.015	0.026484
250	0.06	0.058634
500	0.153	0.122935
1000	0.238	0.251538

### Regression Output:

Constant	-0.00567
Std Err of Y Est	0.02051
R Squared	0.968224
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s) 0.000257  
 Std Err of Coef. 2.69E-05

	Absorbance	COD mg/L
HW1	0.11	449.7074
HW1	0.129	523.5786
RES1	0.131	531.3545
RES2	0.144	581.898
IN1	0.201	803.5117
IN2	0.177	710.2007

# Experiment: 3 Analysis of Residential, Industrial & Raw-composite wastewater & Activated sludge March 2nd, 1993

## C: ATP ANALYSIS

Standrads	Mole/ml	µg/ml	Log
s1	3.84E-08	19.2	1.283301
s2	3.84E-09	1.92	0.283301
s3	3.84E-10	0.192	-0.7167
s4	3.84E-11	0.0192	-1.7167
s5	3.84E-12	0.00192	-2.7167
s6	3.84E-13	0.000192	-3.7167
s7	3.84E-14	1.92E-05	-4.7167
s8	3.84E-15	1.92E-06	-5.7167
s9	3.84E-16	1.92E-07	-6.7167

	RI	RI	Log(RI)
s2	2200	2199.95	3.342413
s3	350	349.95	2.544006
s4	30	29.95	1.476397
s5	4	3.95	0.596597
s6	0.9	0.85	-0.07058
s7	0.55	0.5	-0.30103
s8	0.3	0.25	-0.60206
Sterile w	0.05		
Tris buff	0.06		

Regression Output:	
Constant	2.848274
Std Err of Y Est	0.368038
R Squared	0.950442
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.681088
Std Err of Coef.	0.069553

## E: ATP ANALYSIS

### Light output from wastewater and activated sludge

Grab Sample	sample	Relative intensity
INDUS	1	0.6
INDUS	2	1.4
INDUS	3	1.3
RES	1	1.4
RES	2	1.5
RES	3	1.155
HEAD	1	27
HEAD	2	14
HEAD	3	25
AS	1	41.5
AS	2	36
AS	3	30.5

**Experiment: 3 Analysis of Residential, Industrial & Raw-composite wastewater & Activated sludge March 2nd, 1993**

**E:ATP ANALYSIS**

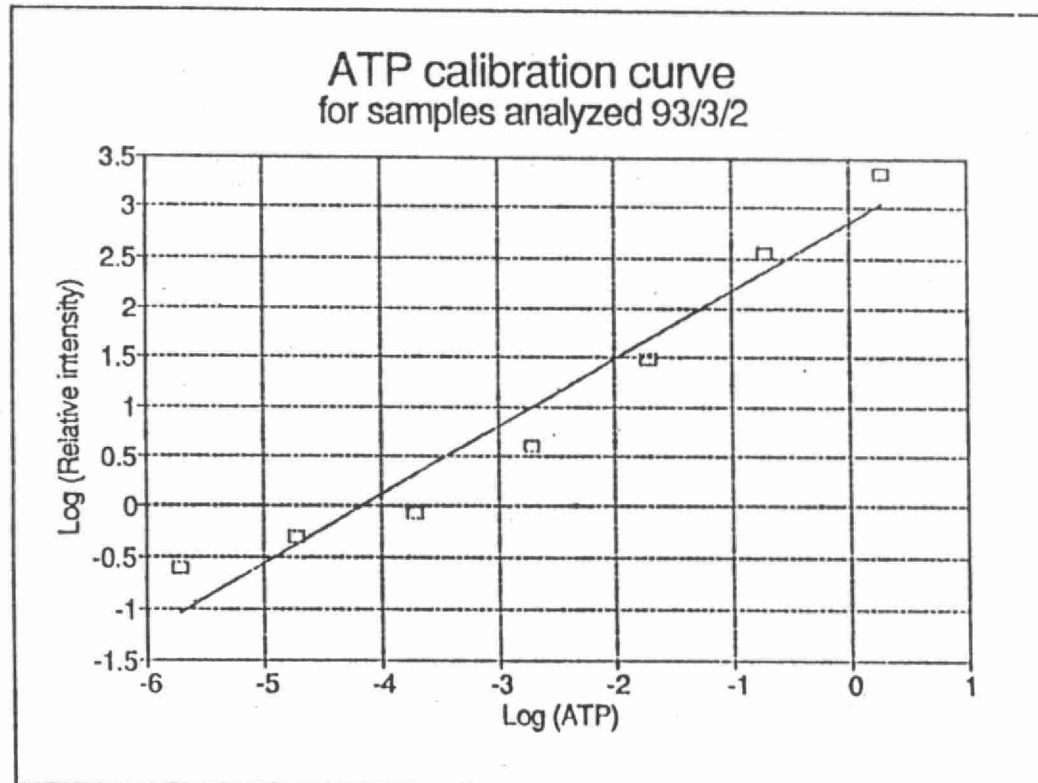
Sample	LogS	Log ATP	ATP	Average µg/ml	Xbio mg/L
INDUS	-0.22185	-4.50767	3.11E-05	7.85E-05	0.10492
INDUS	0.146128	-3.9674	0.000108		
INDUS	0.113943	-4.01465	9.67E-05		
			STD	4.15E-05	
RES	0.146128	-3.9674	0.000108	0.000103	0.137325
RES	0.176091	-3.9234	0.000119		
RES	0.062582	-4.09006	8.13E-05		
			STD	1.95E-05	
HEAD	1.431364	-2.08036	0.008311	0.006301	8.417823
HEAD	1.146128	-2.49916	0.003168		
HEAD	1.39794	-2.12944	0.007423		
			STD	0.0027	
AS	1.618048	-1.80627	0.015622	1.274668	
AS	1.556303	-1.89692	0.012679		
AS	1.4843	-2.00264	0.009939		
			STD	0.0028	

**Experiment: 3 Analysis of Residential, Industrial & Raw-composite wastewater & Activated sludge March 2nd, 1993**

**F: ATP ANALYSIS**

Calibration Curve

Relative intensity versus ATP concentration



**Experiment: 3 Analysis of Residential, Industrial & Raw-composite wastewater & Activated sludge March 2nd, 1993**

**G:TSS, VSS & FIXED SOLIDS ANALYSIS OF WASTEWATER**

**HEADWORKS WASTEWATER**

Sample			TSS			VSS	FSS
	g	g	mg/L	g	mg/L	g	mg/L
1	1.1048	1.1183	270	1.1099	168	0.994	1159
2	1.1069	1.1362	293	1.1103	259	0.9937	1166
3	1.114	1.1197	114	1.1108	178	0.9978	1130
4	1.1022	1.1199	354	1.107	258	0.9907	1163
5	1.1224	1.1259	70	1.1229	60	1.0038	1191
6	1.1049	1.1166	234	1.1063	206	0.994	1123
AVG			222.5				1155.33
STD			99.75				22.89

**INDUSTRIAL SEWER**

Sample			TSS		VSS		FS	
	g	g	mg/L	g	mg/L	g	mg/L	
1	1.1036	1.1148	186.67	1.1044	173.33	0.9914	1883.333	
2	1.1062	1.1212	250	1.1078	223.33	0.9932	1910	
3	1.0995	1.1125	216.67	1.1011	190	0.9865	1910	
4	1.1045	1.117	208.33	1.106	183.33	0.9913	1911.667	
5	1.1057	1.1183	210	1.1078	175	0.9825	2088.333	
6	1.1018	1.1125	178.33	1.1032	155	0.9887	1908.33	
ATP			208.3333		183.3333		1935.278	
STD			23.01368		20.88327		69.14435	



**Experiment: 3 Analysis of Residential, Industrial & Raw-composite wastewater & Activated sludge March 2nd, 1993**

**G: TSS, VSS & FIXED SOLIDS ANALYSIS OF WASTEWATER**

**RESIDENTIAL WASTEWATER**

Sample			TSS		VSS		FS	
	g	g	mg/L	g	mg/L	g	mg/L	
1	1.1006	1.1099	93	1.1013	86	0.9895	1118	
2	1.102	1.1119	99	1.1025	94	0.9904	1121	
3	1.1055	1.1149	94	1.1055	90	0.9961	1098	
4	1.0995	1.1104	109	1.1009	95	0.9878	1131	
5	1.1055	1.1179	124	1.1076	103	0.9937	1139	
6	1.1101	1.1216	115	1.11	96	0.996	1160	
AVG			105.66		94		1127.83	
STD			11.37		5.26		19.16	

**ACTIVATED SLUDGE**

Sample			TSS		VSS		FS	
	g	g	mg/L	g	mg/L	g	mg/L	
1	1.1121	1.1365	2440	1.1176	1890	1.00009	11751	
2	1.1086	1.1355	2690	1.1158	1970	0.9994	11640	
3	1.1066	1.129	2240	1.1121	1690	0.9978	11430	
4	1.108	1.1319	2390	1.1136	1830	0.9983	11530	
5	1.1101	1.1257	1560	1.1136	1210	0.9984	11520	
6	1.1063	1.1274	2110	1.1111	1630	0.9961	11500	
AVG			2238.333		1703.333		11561.83	
STD			352.2034		248.6407		104.7703	

**Experiment: 4 Analysis of Residential, Industrial & Raw composite wastewater & Activated sludge.**  
**March 9th, 1993**

**A:RAW DATA**

**Headworks wastewater**

Collected at GWWTP 9:25 a.m.  
 Dissolved oxygen concentration 8.5 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 12.5°C

pH 7.63

**Industrial wastewater**

Collected at Silvercreek parkway 8:35 a.m.  
 Dissolved oxygen concentration 5.4 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 11.1°C

pH 6.59

**Residential wastewater**

Collected at Burns Drive 8:50 a.m.  
 Dissolved oxygen concentration 8.4 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 13.7°C  
 pH 6.79

**Activated Sludge**

Collected at GWWTP 9:35AM  
 Dissolved oxygen concentration 5.9 mg/L  
 Atmospheric pressure 736 mm Hg  
 wastewater temp 12.3°C  
 pH 6.28

**B:CHEMICAL OXYGEN DEMAND ANALYSIS**

**Calibration Curve**

Sample Absorbance

µg/ml at 600nm Best fit

62.5	0.026	0.044331
125	0.071	0.061536
250	0.101	0.095948
500	0.175	0.16477
1000	0.296	0.302415

Regression Output:

Constant	0.027125
Std Err of Y Est	0.014106
R Squared	0.98663
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s) 0.000275

Std Err of Coef. 1.85E-05

Sample Absorbance

COD

Sample	Absorbance	COD mg/L
HW1	0.15	446.347
HW2	0.154	460.8771
RES1	0.217	689.7264
RES2	0.175	537.1602
IN1	0.094	242.9254
IN2	0.065	137.582

Experiment: 4 Analysis of Residential, Industrial & Raw composite wastewater & Activated sludge.  
March 9th, 1993

C:ATP ANALYSIS

Calibration curve

Standrads	Mole/ml	µg/ml	Log
s1	3.84E-08	19.2	1.283301
s2	3.84E-09	1.92	0.283301
s3	3.84E-10	0.192	-0.7167
s4	3.84E-11	0.0192	-1.7167
s5	3.84E-12	0.00192	-2.7167
s6	3.84E-13	0.000192	-3.7167
s7	3.84E-14	1.92E-05	-4.7167
s8	3.84E-15	1.92E-06	-5.7167
s9	3.84E-16	1.92E-07	-6.7167

Regression Output:

Constant 2.970907

Std Err of Y Est 0.278626

R Squared 0.970922

No. of Observations 6

Degrees of Freedom 4

X Coefficient(s) 0.769736

Std Err of Coef. 0.066604

RI RI log(RI)

s2	2200	2199.95	3.342413
s3	350	349.95	2.544006
s4	30	29.95	1.476397
s5	4	3.95	0.596597
s6	0.9	0.85	-0.07058
s7	0.55	0.5	-0.30103
s8	0.3	0.25	-0.60206
Sterile w	0.05		
Tris	0.05		

D:ATP ANALYSIS

Light output from wastewater or sludge

Grab Sample Realtive  
Sample # intensity

RES 1 0.275

RES 2 0.25

RES 3 0.35

INDUS 1 2.3

INDUS 2 1.7

INDUS 3 1.15

HEAD 1 27.54

HEAD 2 27

HEAD 3 19.5

AS 1 33

AS 2 43

AS 3 27.5

Experiment: 4 Analysis of Residential, Industrial & Raw composite wastewater & Activated sludge.  
March 9th, 1993

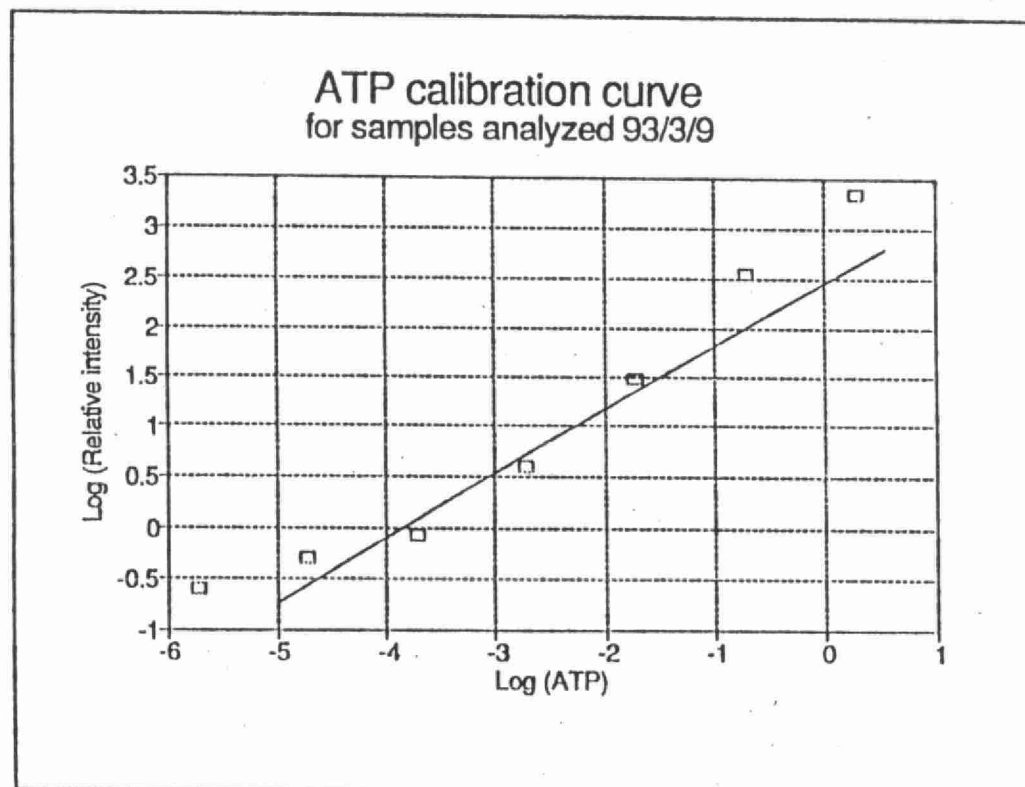
E:ATP ANALYSIS

Samples	Log(S)	Log(ATP)	ATP µg/ml	Average	Xbio mg/L
RES	-0.56067	-4.58803	2.58E-05	2.8E-05	0.045359
RES	-0.60206	-4.64181	2.28E-05		
RES	-0.45593	-4.45196	3.53E-05		
			STD	6.53E-06	
INDUS	0.361728	-3.38971	0.000408	0.000283	0.458468
INDUS	0.230449	-3.56026	0.000275		
INDUS	0.060698	-3.78079	0.000166		
			STD	0.0001	
HEAD	1.439964	-1.98892	0.010258	0.008936	14.48338
HEAD	1.431364	-2.00009	0.009998		
HEAD	1.290035	-2.1837	0.006551		
			STD	0.0021	
AS	1.518514	-1.88687	0.012976	1.383853	
AS	1.633468	-1.73753	0.018301		
AS	1.439333	-1.98974	0.010239		
			STD	0.0041	

Experiment: 4 Analysis of Residential, Industrial & Raw composite wastewater & Activated sludge.  
March 9th, 1993

F: ATP ANALYSIS

Relative intensity versus ATP concentration



**Experiment: 4 Analysis of Residential, Industrial & Raw composite wastewater & Activated sludge.**  
**March 9th, 1993**

**G: TSS, VSS & FIXED SOLIDS ANALYSIS OF WASTEWATER**

**HEADWORKS WASTEWATER**

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L	mg/L	
1	1.103	1.1176	146	1.1052	121	0.9936	1119		
2	1.1034	1.1393	359	1.1072	321	0.9936	1136		
3	1.1072	1.1306	231	1.1117	186	0.9978	1139		
4	1.0999	1.128	281	1.1043	237	0.9904	1139		
5	1.1139	1.134	201	1.118	160	1.0036	1144		
6	1.1043	1.1258	215	1.109	168	0.9936	1154		
118	AVG		238.83		198.83		1138.5		
	STD		66.95		64.63		10.46		

**INDUSTRIAL SEWER**

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L	mg/L	
1	1.1025	1.1134	108	1.1044	89	0.9909	2837.5		
2	1.1031	1.113	99	1.1046	84	0.9927	2797.5		
3	1.0954	1.1051	97	1.0969	82	0.9862	2767.5		
4	1.1011	1.1043	32	1.1017	26	0.9912	2762.5		
5	1.1026	1.1096	70	1.1035	61	0.9921	2785		
6	1.1022	1.1081	59	1.1019	62	0.9885	2835		
AVG			77.5		67.33		2797.5		
STD			26.59		21.37		29.68		

Experiment: 4 Analysis of Residential, Industrial & Raw composite wastewater & Activated sludge.  
March 9th, 1993

G: TSS, VSS & FIXED SOLIDS ANALYSIS OF WASTEWATER

RESIDENTIAL WASTEWATER

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L	mg/L	
1	1.113	1.1229	99	1.1164	65	1.0023		1141	
2	1.1083	1.1215	132	1.1123	92	0.9981		1142	
3	1.1203	1.1344	141	1.1232	112	1.0091		1141	
4	1.1167	1.1283	116	1.1181	102	1.0056		1125	
5	1.1124	1.1237	113	1.1142	95	1.0014		1128	
6	1.1142	1.1361	219	1.1178	183	1.0032		1146	
AVG			136.67			108.1667		1137.17	
STD			39.21			34.40		77.77	

ACTIVATED SLUDGE

Sample			TSS			VSS			FS
	g	g	mg/L	g	mg/L	g	mg/L	mg/L	
1	1.1100	1.1589	4890	1.112	4690	1.0013		11070	
2	1.1084	1.1330	2460	1.1165	1642	0.999		11758	
3	1.1069	1.1520	4510	1.1124	3960	0.9974		11500	
4	1.107	1.1236	1666	1.1154	826	0.9984		11700	
5	1.1075	1.1354	2790	1.1136	2180	0.9983		11530	
6	1.1062	1.1480	4180	1.1124	3560	0.9958		11660	
AVG			3416.12			2809.667		11536.33	
STD			1177.67			1361.175		227.3189	

## **Appendix B: Biofilm Experimental Data**



## Biofilm thickness analysis, May, 1994

### TAG ANALYSIS

LENGTH= 7.9cm  
 DIAMETER= 3.9cm  
 AREA= 144.63cm<sup>2</sup>

TAG #	TRAY g	WET g	DRY g	WATER g	WATER %	B mg/cm <sup>2</sup>	VSS mg/cm <sup>2</sup>	FSS	TSS	VSS/TSS
1	0.9778	3.8179	1.0263	2.7916	73.11873	0.986	0.5572676	0.0566947	0.0122053	45.657962
2	0.9771	3.6584	1.0302	2.6282	71.840149	0.998	0.445261	0.1445024	0.0110486	40.300375
3	0.9699	2.9762	1.0178	1.9584	65.802029	0.9711	0.6457667	0.0082968	0.0065033	99.29832
4	0.971	4.5491	1.1706	3.3785	74.267438	1.1	0.9762554	0.8919047	0.0152654	63.952172
5	0.9771	3.748	1.0312	2.7168	72.48666	0.9781	0.7342657	0.006914	0.0116542	63.004271
6	0.9712	3.941	1.0998	2.8412	72.093377	1.0133	1.1961203	0.291079	0.01204	99.345354
				AVG	71.601397	0.759	0.233	0.011	68.593	
				STD	2.9707061	0.280	0.340	0.003	25.565	

### MEASUREMENTS

THICK mm	XF mg/cm <sup>3</sup>	Best fit B	Regression Output:	
0.21	26.536552	0.439932	Constant	-0.318978
0.24	18.55254	0.5483477	Std Err of Y Est	0.1699176
0.29	22.267816	0.7290406	R Squared	0.7045102
0.32	30.507981	0.8374564	No. of Observations	6
0.35	20.979021	0.9458721	Degrees of Freedom	4
0.38	31.476849	1.0542878		
AVG	0.298	25.05346	X Coefficient(s)	3.6138578
STD	0.0652	5.2883668	Std Err of Coef.	1.1702231

TABLE B-1 GUELPH MONTHLY WATER POLLUTION CONTROL STATISTICS

DATE	Volatile suspended solids of raw wastewater (mg/L)
02/02/1994	294
02/08/1994	254
02/15/1994	294
03/01/1994	438
03/09/1994	254
03/16/1994	184
03/23/1994	149
04/6/1994	267
04/19/1994	350
04/25/1994	240
05/10/1994	292
05/18/1994	449

TABLE B-2 BIOFILM THICKNESS & VSS OF SCRAPINGS

Date	Biofilm thickness on tag  Toluene	Biofilm thickness on tag  Toluene & Perc	Biofilm thickness on tag  Perc	Volatile suspended solids of scrapings mg/L
02/02/1994	0.55		0.27	
02/15/1994	0.167	0.287		
03/01/1994	0.288		0.788	
03/23/1994	0.456	0.497		
04/06/1994	0.218	0.237		1237.5
04/19/1994	0.127,0.218			775
04/25/1994	0.32,0.267			964
05/18/1994	0.46			

# VOC headspace analysis, experimental data for February 2nd, 1994.

Initial reactor concentration for toluene 0.96 mg/L, PCE concentration 5.3 mg/L, all reactor contain wastewater.  
reactor 1, toluene & tag, reactor 2, PCE & tag, reactor 3, toluene & PCE.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	21739	0.866	0.83226	-0.03374	0.001138
S2	9212	0.433	0.352674	-0.08033	0.006452
S3	1596	0.0866	0.061102	-0.0255	0.00065

STDS 0.003218

### Regression Output:

Constant	0.046522
Std Err of Y Est	0.04181
R Squared	0.994268
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 3.83E-05  
Std Err of Coef. 2.91E-06

## TOLUENE CONCENTRATION IN REACTOR 1

Time	AREA	CONC	AVERAGE
hrs	CHRIS	mg/L	mg/L
7	14092	0.586022	
12	15705	0.647775	0.641037
12	15353	0.634299	
19	10483	0.447855	0.558075
19	16241	0.668295	
22.5	15077	0.623732	0.623005
22.5	15039	0.622277	
26	13602	0.567263	0.564219
26	13443	0.561176	
29.5	12748	0.534568	0.542015
29.5	13137	0.549461	
35	11950	0.504018	0.47808
35	10595	0.452142	
44	8486	0.371401	0.366826
44	8247	0.362251	
48	7156	0.320483	0.319067
48	7082	0.31765	

## TOLUENE CONCENTRATION IN REACTOR 1

TIME	AREA	CONC	Average
hrs		mg/L	mg/L
0	16242	0.668333	0.639888
0	14756	0.611443	
3.5	15126	0.625608	0.631734
3.5	15446	0.637859	
7	14333	0.595249	0.590636

## TOLUENE CONCENTRATION IN REACTOR 3

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	16890	0.693141	0.683704
0	16397	0.674267	
3.5	16315	0.671128	0.589908

# VOC headspace analysis, experimental data for February 2nd, 1994.

Initial reactor concentration for toluene 0.96 mg/L., PCE concentration 5.3 mg/L, all reactor contain wastewater.  
reactor 1, toluene & tag, reactor 2, PCE & tag, reactor 3, toluene & PCE.

## TOLUENE CONCENTRATION IN REACTOR 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
3.5	12072	0.508688	
7	17080	0.700415	0.610907
7	12404	0.521399	
12	16274	0.669558	0.683972
12	17027	0.698386	
19	16321	0.671358	0.603499
19	12776	0.53564	
22.5	11838	0.49973	0.500936
22.5	11901	0.502142	
26	12053	0.507961	0.497528
26	11508	0.487096	
29.5	14148	0.588166	0.584663
29.5	13965	0.58116	
35	10400	0.444677	0.511885
35	13911	0.579093	
44	13369	0.558343	0.554782
44	13183	0.551222	
48	12824	0.537478	0.488149
48	10247	0.43882	

## PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	35232	9.72	9.690533	-0.02947	0.000868
S2	13528	4.86	4.943925	0.083925	0.007043
S4	1784	2.43	2.375542	-0.05446	0.002966

STDS 0.00314

### Regression Output:

Constant	1.985386
Std Err of Y Est	0.104294
R Squared	0.999605
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 0.000219  
Std Err of Coef. 4.35E-06

## PERC CONCENTRATION IN REACTOR 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	34068	9.435969	9.311312
0	32928	9.186654	
3.5	30973	8.759101	7.669878
3.5	21012	6.580656	

VOC headspace analysis, experimental data for February 2nd, 1994.

Initial reactor concentration for toluene 0.96 mg/L., PCE concentration 5.3 mg/L, all reactor contain wastewater.  
reactor 1, toluene & tag, reactor 2, PCE & tag, reactor 3, toluene & PCE.

PERC CONCENTRATION IN REACTOR 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
7	32161	9.018913	7.809845
7	21104	6.600776	
12	30309	8.613886	8.788734
12	31908	8.963583	
19	30138	8.576488	7.783164
19	22883	6.989839	
22.5	19515	6.253266	6.169724
22.5	18751	6.086181	
26	19218	6.188313	6.095038
26	18365	6.001764	
29.5	25617	7.587758	7.549267
29.5	25265	7.510776	
35	17381	5.786566	6.576063
35	24601	7.365561	
44	25118	7.478628	7.384041
44	24253	7.289454	
48	24489	7.341067	6.701158
48	18637	6.06125	

PERC CONCENTRATION IN REACTOR 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
3.5	27075	7.906618	
7	28190	8.150466	8.080264
7	27548	8.010062	
12	26928	7.87447	7.601973
12	24436	7.329476	
19	25741	7.614876	6.741071
19	17750	5.867265	
22.5	25467	7.554953	7.402193
22.5	24070	7.249433	
26	17926	5.905756	6.389077
26	22346	6.872398	
29.5	16503	5.594549	6.462341
29.5	24439	7.330132	
35	20110	6.383391	6.529918
35	21450	6.676445	
44	17717	5.860048	5.993125
44	18934	6.126203	
48	22299	6.86212	7.101593
48	24489	7.341067	

PERC CONCENTRATION IN REACTOR 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	24607	7.366873	8.142046
0	31696	8.917219	
3.5	30805	8.72236	8.314489

# VOC headspace analysis, experimental data for February 8th, 1994.

Initial reactor concentration for toluene 0.96 mg/L., reactor contents, wastewater and toluene.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S5	28943	1.732	1.7267	-0.005	0.00002
S1	17402	0.866	1.0382	0.1722	0.02966
S2	6442	0.433	0.3843	-0.049	0.00237
S3	2855	0.0866	0.1703	0.0837	0.00701
S4	1505	0.0433	0.0898	0.0465	0.00216

STDS 0.0122375

### Regression Output:

Constant	-0.049702
Std Err of Y Est	0.0981033
R Squared	0.9851812
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s) 0.0000597  
Std Err of Coef. 0.0000042

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	23246	1.3371625	1.472681
0	27789	1.6081995	
3.5	27098	1.5669742	1.5316553
3.5	25914	1.4963363	
7	42983	2.5146789	2.4751837
7	41659	2.4356886	
10.5	24934	1.4378692	1.2091016

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
10.5	17265	0.9803339	
16.5	26169	1.5115497	1.5094616
16.5	26099	1.5073735	
22.5	26011	1.5021234	1.4030275
22.5	22689	1.3039317	
28.5	22426	1.288241	1.3688422
28.5	25128	1.4494433	
45.75	10012	0.5476174	0.4955041
45.75	8265	0.4433908	
51.75	6080	0.3130329	0.2577278
51.75	4226	0.2024226	
68	2288	0.0868009	0.09047
68	2411	0.0941391	
73	34813	2.0272538	1.9723663
73	32973	1.9174788	
90	13664	0.765497	0.6566169
90	10014	0.5477367	
95	9077	0.491835	0.5359836
95	10557	0.5801323	

# VOC headspace analysis experimental data, for February 15th, 1994

Initial concentration of toluene 0.96 mg/L, PCE 5.3 mg/L. reactors all contain wastewater, reactor 1, toluene & tag, reactor 2 toluene, PCE & tag, reactor 3 toluene and PCE.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S5	46793	1.732	1.7426	0.0106	0.0001
S1	18006	0.866	0.6707	-0.195	0.0382
S2	10944	0.433	0.4076	-0.025	0.0006
S3	2082	0.0866	0.0775	-0.009	0.0001
S4	1459	0.0433	0.0543	0.0110	0.0001
STDS				0.01697	

### Regression Output:

Constant	0.0416499
Std Err of Y Est	0.1008023
R Squared	0.9843546
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	0.0000372
Std Err of Coef.	0.0000027

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME	AREA	CONC	Average
hrs		mg/L	mg/L
0	16704	0.663731	0.6304371
0	14916	0.5971432	
3	12742	0.5161804	0.5828425
3	16322	0.6495047	
7	13584	0.5475376	0.5717446
7	14884	0.5959515	
17	10883	0.4469485	0.5201466

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME	AREA	CONC	Average
hrs		mg/L	mg/L
17	14814	0.5933446	
22	15156	0.6060812	0.5780198
22	13649	0.5499583	
25	14551	0.5835501	0.581297
25	14430	0.5790439	
30	13987	0.5625459	0.5021962
30	10746	0.4418464	
40	11719	0.4780824	0.4623851
40	10876	0.4466878	
46	7548	0.3227483	0.3442552
46	8703	0.3657622	
49	8337	0.3521318	0.3282973
49	7057	0.3044627	
56.5	7555	0.323009	0.2809448
56.5	5296	0.2388806	
67	6713	0.2916517	0.2704241
67	5573	0.2491964	
72	6538	0.2851344	0.2775186
72	6129	0.2699027	
78	20542	0.8066636	0.7949698
78	19914	0.783276	
83	20439	0.8028277	0.7747105
83	18929	0.7465932	
93	28374	1.0983386	1.0983386
93	28374	1.0983386	
99	24697	0.9614018	0.9391314
99	23501	0.916861	



# VOC headspace analysis experimental data, for February 15th, 1994

Initial concentration of toluene 0.96 mg/L, PCE 5.3 mg/L. reactors all contain wastewater, reactor 1, toluene & tag, reactor 2 toluene, PCE & tag, reactor 3 toluene and PCE.

## TOLUENE CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	Average mg/L
0	18354	0.7251793	0.7133366
0	17718	0.7014938	
3	17656	0.6991848	0.7084393
3	18153	0.7176938	
7	17825	0.7054786	0.6998365
7	17522	0.6941945	
17	16585	0.6592992	0.6588337
17	16560	0.6583682	
22	11297	0.4623665	0.4560354
22	10957	0.4497044	
25	15616	0.6232123	0.6342916
25	16211	0.6453709	
30	14181	0.5697708	0.6050571
30	16076	0.6403433	
40	12107	0.492532	0.5305928
40	14151	0.5686535	
46	11502	0.470001	0.4776913
46	11915	0.4853817	
49	10660	0.4386437	0.4525906
49	11409	0.4665375	
56.5	8256	0.3491152	0.3558746
56.5	8619	0.3626339	
67	6033	0.2663275	0.2489916
67	5102	0.2316557	
72	5430	0.2438709	0.254913
72	6023	0.2659551	
78	18380	0.7261476	0.8164209
78	23228	0.9066941	
83	21949	0.8590623	0.9146079
83	24932	0.9701536	

## TOLUENE CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	Average mg/L
93	24234	0.944159	0.7627746
93	14493	0.5813901	
99	21076	0.8265505	0.8592299
99	22831	0.8919093	

## PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S5	70568	19.72	20.357	0.6372	0.40601
S1	25906	9.72	7.6107	-2.109	4.44923
S2	16590	4.86	4.9519	0.0919	0.00844
S6	9798	2.43	3.0135	0.5835	0.34042
S3	3607	0.972	1.2465	0.2745	0.07538
S4	2772	0.486	1.0082	0.5222	0.27274

STDS 1.7331394

## Regression Output:

Constant	0.217113
Std Err of Y Est	1.1781602
R Squared	0.9795126
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	0.0002854
Std Err of Coef.	0.0000206

# VOC headspace analysis experimental data, for February 15th, 1994

Initial concentration of toluene 0.96 mg/L, PCE 5.3 mg/L. reactors all contain wastewater, reactor 1, toluene & tag, reactor 2 toluene, PCE & tag, reactor 3 toluene and PCE.

## PERC CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	36251	10.563132	10.446974
0	35437	10.330817	
3	32968	9.626165	9.7971194
3	34166	9.9680737	
7	32621	9.5271314	9.4322361
7	31956	9.3373407	
17	29268	8.5701867	8.4898468
17	28705	8.4095068	
22	18256	5.427367	5.3157758
22	17474	5.2041846	
25	27362	8.0262152	8.1366648
25	28136	8.2471145	
30	23913	7.0418722	7.7309694
30	28742	8.4200666	
40	23742	6.9930689	7.4068982
40	26642	7.8207276	
46	24189	7.1206425	7.1850001
46	24640	7.2493577	
49	24087	7.0915317	7.2303786
49	25060	7.3692255	
56.5	22583	6.6622908	6.8007096
56.5	23553	6.9391284	
67	21399	6.3243778	5.6889357
67	16946	5.0534936	
72	21598	6.3811723	6.7203696
72	23975	7.059567	
78	38628	11.241526	13.029269
78	51156	14.817012	
83	48370	14.021889	14.903203
83	54546	15.784516	

## PERC CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
93	53795	15.570181	11.931908
93	28299	8.2936346	
99	46186	13.398576	13.900309
99	49702	14.402041	

## PERCHLOROETHYLENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	31076	9.0861891	8.5594843
0	27385	8.0327794	
3	20817	6.1582752	7.1919924
3	28061	8.2257095	
7	22077	6.5178787	6.8566479
7	24451	7.1954172	
17	15890	4.7521117	5.8464762
17	23559	6.9408408	
22	23954	7.0535736	6.6624335
22	21213	6.2712935	
25	23117	6.8146942	6.7657482
25	22774	6.7168021	
30	22389	6.6069233	5.7251814
30	16210	4.8434395	
40	21280	6.2904152	6.0645215
40	19697	5.8386277	
46	14400	4.3268664	4.737699
46	17279	5.1485317	
49	17678	5.2624061	4.7870731
49	14347	4.3117402	

# **VOC headspace analysis experimental data, for February 15th, 1994**

Initial concentration of toluene 0.96 mg/L, PCE 5.3 mg/L. reactors all contain wastewater, reactor 1, toluene & tag, reactor 2 toluene, PCE & tag, reactor 3 toluene and PCE.

## **PERCHLOROETHYLENE CONCENTRATION IN REACTOR # 2**

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
56.5	14552	4.3702471	3.641194
56.5	9443	2.9121409	
67	5124	1.6795002	1.5326622
67	4095	1.3858241	
72	0	0.217113	0.217113
72	0	0.217113	
78	17516	5.2161713	5.1068633
78	16750	4.9975553	
83	26077	7.6594768	5.9390884
83	14021	4.2187	
93	31263	9.1395588	9.1395588
93	31263	9.1395588	
99	10890	3.325114	3.2494831
99	10360	3.1738522	

## **PERC CONCENTRATION IN REACTOR # 1**

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	36732	10.700409	10.530596
0	35542	10.360783	
3	33219	9.6978003	8.7134573
3	26321	7.7291143	
7	31146	9.1061671	8.4945559
7	26860	7.8829447	
17	30588	8.9469141	8.2974875
17	26037	7.6480608	
22	29692	8.6911962	7.9024945
22	24165	7.1137929	

## **PERC CONCENTRATION IN REACTOR # 1**

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
25	31255	9.1372756	8.7671124
25	28661	8.3969492	
30	19374	5.7464437	5.6054563
30	18386	5.4644689	
40	28870	8.4565977	7.5104983
40	22240	6.5643988	
46	27319	8.013943	7.2566354
46	22012	6.4993277	
49	25947	7.6223749	7.9076317
49	27946	8.1928886	
56.5	25769	7.5715738	6.7008198
56.5	19667	5.8300658	
67	20839	6.164554	6.3362218
67	22042	6.5078897	
72	22970	6.7727404	6.835671
72	23411	6.8986016	
78	21558	6.3697563	5.6044574
78	16195	4.8391586	
83	19320	5.7310321	5.7310321
83	19320	5.7310321	
93	12693	3.8396894	3.8244205
93	12586	3.8091516	
99	9325	2.8784637	3.1377492
99	11142	3.3970347	

# VOC headspace analysis experimental data, for February 15th, 1994

Initial concentration of toluene 0.96 mg/L, PCE 5.3 mg/L. reactors all contain wastewater, reactor 1, toluene & tag, reactor 2 toluene, PCE & tag, reactor 3 toluene and PCE.

## DISSOLVED OXYGEN & TEMPERATURE

### REACTOR # 1

TIME hrs	DO mg/L	TEMP °C
0	6.5	22.3
17	5.3	21
40	4.5	21.3
67	4.2	20.9
99	4	21

### REACTOR # 2

132	TIME hrs	DO mg/L	TEMP °C
	0	6.7	22.1
	17	5.5	21.2
	40	4.4	21.1
	67	4.3	20.9
	99	3.9	21.4

### REACTOR # 3

TIME hrs	DO mg/L	TEMP °C
0	6.1	22
17	5.5	21.3
40	4.2	21.5
67	4	21
99	4.1	21.3

# VOC headspace analysis, experimental data for March 1st, 1994.

Initial reactor concentration for toluene 9.6 mg/L., PCE concentration, 5.3 mg/L, all reactors contain wastewater, reactor 1, toluene & tag, reactor 2, toluene & PCE, reactor 3, PCE & tag.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Standard	AREA	CONC	FIT	ERR	ERR2
S1	212747	17.3	15.02674	-2.27326	5.167689
S2	122899	8.66	8.680601	0.020601	0.000424
S6	23195	4.33	1.638309	-2.69169	7.2452
S3	9403	1.733	0.664153	-1.06885	1.142435

STDS 3.394285

### Regression Output:

Constant	1.503298
Std Err of Y Est	1.502686
R Squared	0.967666
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s) 7.06E-05

Std Err of Coef. 9.13E-06

## TOLUENE CONCENTRATION IN REACTOR # 1

Time	AREA	CONC	Average
hrs	mg/L	mg/L	
0	337262	25.32479	23.06103
0	273162	20.79727	
4	293688	22.24707	19.30373
4	210345	16.36038	
8	348348	26.10781	24.13245

## TOLUENE CONCENTRATION IN REACTOR # 1

Time	AREA	CONC	Average
hrs	mg/L	mg/L	
8	292414	22.15708	
11	339739	25.49974	23.27794
11	276827	21.05614	
30	262540	20.04702	20.91417
30	287094	21.78132	
33.5	296909	22.47457	22.74403
33.5	304539	23.01349	
39.5	297304	22.50247	21.37759
39.5	265452	20.2527	
46	214744	16.67109	15.46071
46	180471	14.25032	
54	153588	12.35152	12.94215
54	170312	13.53277	
58	102607	8.750635	8.641897
58	99528	8.533159	
64	59056	5.674541	5.664688
64	58777	5.654835	
69	19079	2.850886	2.832839
69	18568	2.814793	
78	18533	2.812321	2.722865
78	16000	2.63341	

# VOC headspace analysis, experimental data for March 1st, 1994.

Initial reactor concentration for toluene 9.6 mg/L., PCE concentration, 5.3 mg/L., all reactors contain wastewater, reactor 1, toluene & tag, reactor 2, toluene & PCE, reactor 3, PCE & tag.

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA mg/L	CONC mg/L	AVERAGE mg/L
0	311944	23.53652	24.35918
0	335238	25.18183	
4	335859	25.22569	20.79304
4	210345	16.36038	
8	237693	18.29203	18.84836
8	253446	19.40469	
11	314416	23.71113	23.76756
11	316014	23.824	
30	311638	23.51491	24.08657
30	327825	24.65823	
33.5	310237	23.41596	22.47312
33.5	283540	21.53029	
39.5	309583	23.36976	21.29989
39.5	250973	19.23002	
46	186213	14.65589	16.34778
46	234120	18.03966	
54	130337	10.70926	12.93113
54	193251	15.153	
58	167253	13.31671	14.12287
58	190080	14.92903	
64	135185	11.05168	11.30359
64	142318	11.5555	
69	92839	8.060702	8.271008
69	98794	8.481315	
78	52404	5.204697	4.955578
78	45350	4.706459	

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA mg/L	CONC mg/L	AVERAGE mg/L
81.5	32895	3.826737	4.097152
81.5	40552	4.367567	

## PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Standard	AREA	CONC	FIT	ERR	ERR2
S1	32401	9.72	8.96285	-0.75715	0.573276
S2	19928	4.86	6.127384	1.267384	1.606263
S4	1419	2.43	1.919765	-0.51023	0.260339

STDS 0.704332

## Regression Output:

Constant	1.597187
Std Err of Y Est	1.562011
R Squared	0.911458
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 0.000227  
Std Err of Coef. 7.09E-05

VOC headspace analysis, experimental data for March 1st, 1994.

Initial reactor concentration for toluene 9.6 mg/L., PCE concentration, 5.3 mg/L, all reactors contain wastewater, reactor 1, toluene & tag, reactor 2, toluene & PCE, reactor 3, PCE & tag.

PERC CONCENTRATION IN REACTOR # 3

Time hrs	AREA CONTROL	CONC mg/L	AVERAGE mg/L
0	36342	9.858751	8.902267
0	27927	7.945783	
4	28095	7.983975	8.40044
4	31759	8.816905	
8	3298	2.346915	5.780368
8	33505	9.21382	
11	33327	9.173356	8.53911
11	27747	7.904864	
30	31040	8.653456	7.995341
30	25250	7.337226	
33.5	22810	6.782545	7.160478
33.5	26135	7.538411	
39.5	27249	7.791655	7.848601
39.5	27750	7.905546	
46	28320	8.035123	7.713568
46	25491	7.392012	
54	25509	7.396104	6.820622
54	20446	6.245141	
58	20761	6.316749	6.69491
58	24088	7.07307	
64	23785	7.00419	6.816985
64	22138	6.62978	
69	22274	6.660697	6.681383
69	22456	6.70207	
78	22885	6.799594	6.608525
78	21204	6.417455	

PERC CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	35130	9.583229	9.618692
0	35442	9.654155	
4	25814	7.465439	7.580694
4	26828	7.69595	
8	23809	7.009646	7.014078
8	23848	7.018511	
11	16111	5.259672	5.858114
11	21376	6.456556	
30	18143	5.721604	5.743086
30	18332	5.764569	
33.5	17830	5.65045	5.614759
33.5	17516	5.579069	
39.5	15904	5.212616	4.772281
39.5	12030	4.331946	
46	14542	4.902994	4.593146
46	11816	4.283298	
54	15431	5.105089	4.964828
54	14197	4.824566	
58	15380	5.093495	4.578483
58	10849	4.063471	
64	13091	4.573141	4.6643
64	13893	4.755458	
69	14535	4.901403	4.86253
69	14193	4.823657	
78	0	1.597187	1.597187
78	0	1.597187	

**VOC headspace analysis, experimental data for March 1st, 1994.**

Initial reactor concentration for toluene 9.6 mg/L., PCE concentration, 5.3 mg/L, all reactors contain wastewater, reactor 1, toluene & tag, reactor 2, toluene & PCE, reactor 3, PCE & tag.

**REACTOR # 1**

TIME	DO	pH	Temp
0	5.4	7.42	21.5
8	4.2	6.3	21.9
30	4.2	6.5	21.7
54	3.4	6.03	21.6
78	3.7	5.89	20.3

**REACTOR # 2**

TIME	DO	pH	Temp
0	4.5	7.82	23.2
8	3.8	7.56	22.6
30	4	7.17	20.9
54	4.2	7.29	20.6
78	5.1	6.67	23.1

**REACTOR # 3**

TIME	DO	pH	Temp
0	4.5	7.83	23.2
8	3.4	7.53	22.1
30	3	7.42	21.9
54	4.1	7.32	20.3
78	4.5	6.60	22.1



VOC headspace analysis, experimental data, for March 9th, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 wastewater,

reactor 1 toluene & MCI slime layers, reactor 2 PCE & MCI slime layers, reactor 3 toluene and PCE.

PERC CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	33845	12.131451	11.864097
0	32382	11.596743	
4	25183	8.9655969	7.687852
4	18191	6.4101072	
7.5	27321	9.7470096	9.9546066
7.5	28457	10.162204	
16.5	28999	10.360298	10.213372
16.5	28195	10.066446	
20.5	31389	11.233813	10.611936
20.5	27986	9.9900589	
25.5	27079	9.6585615	10.132782
25.5	29674	10.607002	
31.5	30059	10.747715	9.8184624
31.5	24974	8.88921	
40.5	27075	9.6570996	9.624023
40.5	26894	9.5909463	
46.5	27216	9.7086334	9.7086334
46.5	27216	9.7086334	
55.5	21662	7.6787148	8.5913376
55.5	26656	9.5039603	
64.5	15406	5.392224	7.2832572
64.5	25754	9.1742904	
71.5	24892	8.85924	8.0597357
71.5	20517	7.2602315	
94	23697	8.4224823	7.8894185

PERC CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
94	20780	7.3563547	

PERC CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	30667	10.969931	12.019429
0	36410	13.068927	
4	31518	11.280961	10.421883
4	26817	9.5628038	
7.5	21055	7.4568638	7.9773183
7.5	23903	8.4977727	
16.5	25092	8.9323375	8.9416575
16.5	25143	8.9509774	
20.5	28588	10.210082	9.8838847
20.5	26803	9.557687	
25.5	23122	8.2123268	8.5379764
25.5	24904	8.8636259	
31.5	24424	8.6881918	7.9124442
31.5	20179	7.1366966	
40.5	22716	8.0639388	7.9583129
40.5	22138	7.852687	
46.5	15350	5.3717567	5.8843531
46.5	18155	6.3969496	

**VOC headspace analysis, experimental data, for March 9th, 1994.**

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L., reactor contents, 1, 2 & 3 wastewater,  
reactor 1 toluene & MCI slime layers, reactor 2 PCE & MCI slime layers, reactor 3 toluene and PCE.

**PERC CONCENTRATION IN REACTOR # 2**

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
55.5	6840	2.2614566	2.2651115
55.5	6860	2.2687664	
64.5	775	0.0447739	0.0447739
64.5	775	0.0447739	
71.5	1049	0.1449175	0.1266432
71.5	949	0.1083688	

**REACTOR # 2**

TIME hrs	DO mg/L	pH	Temp °C
0	4.8	7.75	20.7
16.5	3.2	6.49	21.9
40.5	3.8	6.27	20.6
64.5	3	6.27	20.6
94	2.7	6.09	22.7

**REACTOR # 3**

TIME hrs	DO mg/L	pH	Temp °C
0	4.5	7.82	23.2
16.5	3.8	7.56	22.6
40.5	4	7.17	20.9
64.5	4.2	7.29	20.6
94	5.1	6.67	23.1

**REACTOR # 1**

TIME hrs	DO mg/L	pH	Temp °C
0	5.4	7.42	21.5
16.5	4.2	6.3	21.9
40.5	4.2	6.5	21.7
64.5	3.4	6.03	21.6
94	3.7	5.89	20.3

# VOC headspace analysis experimental data, for March 16, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 wastewater, reactors 2 & 3, MCI slime layers.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	529822	34.34	37.6297	3.28973	10.822311
S2	184808	8.66	13.1256	4.46568	19.942311
S6	98979	4.33	7.02982	2.69982	7.2890237

STDS 6.5289636

## Regression Output:

Constant	-3.485076
Std Err of Y Est	1.2713678
R Squared	0.9969286
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 0.000071

Std Err of Coef. 0.0000039

## TOLUENE CONCENTRATION IN REACTOR #1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	337835	20.509094	20.037428
0	324553	19.565762	
4	317882	19.091965	19.172754
4	320157	19.253543	
11.5	341937	20.800432	20.800432
11.5	341937	20.800432	
20.5	258576	14.879855	16.892053

## TOLUENE CONCENTRATION IN REACTOR #1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
20.5	315239	18.90425	
39.5	192032	10.153678	9.1076816
39.5	162577	8.0616853	
43	114335	4.6353773	5.9280731
43	150737	7.220769	
49	92018	3.0503494	2.3368135
49	71925	1.6232775	
54.5	39014	-0.714172	-0.610442
54.5	41935	-0.506713	
63.5	9249	-2.828181	-2.906627
63.5	7040	-2.985072	
67.5	10856	-2.714047	-2.952117
67.5	4152	-3.190187	

## TOLUENE CONCENTRATION IN REACTOR #3

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	350542	21.411587	19.629718
0	300365	17.847849	
4	278003	16.259625	16.259625
4	278003	16.259625	
11.5	259639	14.955353	14.482053
11.5	246311	14.008754	
20.5	259639	14.955353	14.482053
20.5	246311	14.008754	
39.5	158606	7.7796516	9.3331096

VOC headspace analysis experimental data, for March 16, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 wastewater, reactors 2 & 3, MCI slime layers.

TOLUENE CONCENTRATION IN REACTOR #3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
39.5	202351	10.886568	
43	189239	9.9553096	10.301193
43	198979	10.647077	
49	219071	12.074078	14.185424
49	278526	16.296771	
54.5	159245	7.8250355	6.5088665
54.5	122182	5.1926975	
63.5	106788	4.0993642	6.3312016
63.5	169636	8.5630391	
67.5	137704	6.2951218	6.4262309
67.5	141396	6.5573399	

TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
43	275706	16.096485	
49	216291	11.876633	12.173759
49	224658	12.470885	
54.5	222320	12.304833	12.292013
54.5	221959	12.279193	
63.5	185652	9.7005489	10.771403
63.5	215807	11.842258	
67.5	171033	8.6622587	9.9696563
67.5	207849	11.277054	

TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	355679	21.776434	20.61151
0	322875	19.446585	
4	296882	17.600475	18.353749
4	318094	19.107022	
11.5	331818	20.081746	20.081746
11.5	331818	20.081746	
20.5	241812	13.68922	13.68922
20.5	241812	13.68922	
39.5	230479	12.884312	13.32004
39.5	242749	13.755769	
43	262742	15.175738	15.636111

# VOC headspace analysis experimental data, for March 16, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 wastewater, reactors 2 & 3, MCI slime layers.

## PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	45402	9.72	9.7171	-0.0030	0.0000086
S2	23174	4.86	4.9459	0.08593	0.0073843
S3	22387	4.86	4.7771	-0.0830	0.0068879
STDS					0.0041225

### Regression Output:

Constant	-0.028252
Std Err of Y Est	0.1195027
R Squared	0.9990931
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 0.0002146  
Std Err of Coef. 0.0000065

## PERC CONCENTRATION IN REACTOR # 3

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	36445	7.7944861	7.2302917
0	31188	6.6660972	
4	22911	4.8894804	4.8894804
4	22911	4.8894804	
11.5	18621	3.9686533	3.8619747
11.5	17627	3.7552961	

## PERC CONCENTRATION IN REACTOR # 3

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
39.5	16351	3.4814091	3.134972
39.5	13123	2.7885349	
43	13068	2.7767295	2.8949989
43	14170	3.0132683	
49	22747	4.8542786	6.0671303
49	34048	7.279982	
54.5	10995	2.3317703	2.0299794
54.5	8183	1.7281885	
63.5	6323	1.3289488	1.8872405
63.5	11525	2.4455322	
67.5	6221	1.307055	1.3749902
67.5	6854	1.4429253	

## PERC CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	37960	8.1196733	7.7757047
0	34755	7.431736	
4	33345	7.1290865	7.1447556
4	33491	7.1604247	
11.5	34308	7.3357897	7.3357897
11.5	34308	7.3357897	
39.5	26306	5.6182002	5.2093015
39.5	22496	4.8004027	
43	20168	4.3007091	5.0006665
43	26690	5.7006239	

**VOC headspace analysis experimental data, for March 16, 1994.**

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 wastewater, reactors 2 & 3, MCI slime layers.

**PERC CONCENTRATION IN REACTOR # 1**

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
49	33664	7.1975583	5.8914434
49	21494	4.5853284	
54.5	21600	4.6080808	4.7204474
54.5	22647	4.8328141	
63.5	23387	4.9916514	4.734614
63.5	20992	4.4775766	
67.5	23648	5.0476738	4.512993
67.5	18666	3.9783123	

**REACTOR # 3**

TIME	DO	pH	Temp
0	4.7	7.51	22.9
18.5	5	6.75	21.3
30.5	4.2	6.35	21.8
54.5	2.9	6.93	23.6

**REACTOR # 1**

TIME	DO	pH	Temp
0	4.9	7.57	22
18.5	5.1	7.97	21.8
30.5	4	7.2	21
54.5	3.7	7.92	23.3

**REACTOR # 2**

TIME	DO	pH	Temp
0	4.3	7.44	22.3
18.5	4.2	6.93	21.6
30.5	4.1	6.98	21.2
54.5	2.7	6.92	23.2

# VOC headspace analysis, experimental data for March 23rd ,1994.

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents 1, wastewater,toluene & tag, reactor 2, wastewater, toluene and PCE & tag, reactor 3, wastewater & toluene.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	952755	34.64	33.013	-1.6265	2.64556
S2	457754	17.32	15.861	-1.4586	2.12744
S4	77578	4.33	2.6881	-1.6419	2.69577

STDS 0.31464

## Regression Output:

Constant	1.5756572
Std Err of Y Est	0.1438084
R Squared	0.9999553
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 0.0000347  
Std Err of Coef. 0.0000002

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	317616	12.581225	13.063492
0	345452	13.545758	
6	334784	13.176106	13.894325
6	376239	14.612544	
9	300363	11.983399	11.839704
9	292069	11.696008	
12	308506	12.265559	13.103288

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
12	356859	13.941017	
16	269253	10.905421	11.43547
16	299847	11.96552	
22	323699	12.792005	12.972309
22	334106	13.152613	
25.5	344425	13.510172	12.065019
25.5	261012	10.619866	
35.5	224818	9.3657239	9.3657239
35.5	224818	9.3657239	
40.5	175138	7.6442847	7.3145674
40.5	156107	6.9848502	
50.5	123602	5.8585341	5.7741254
50.5	118730	5.6897167	
54	89993	4.6939639	4.2897999
54	66665	3.8856359	
64	1643	1.6325881	1.6307863
64	1539	1.6289844	

## TOLUENE CONCENTRATION IN REACTOR # 3

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	302886	12.070823	11.653682
0	278809	11.236542	
6	266239	10.800984	11.212009
6	289963	11.623034	
9	292914	11.725288	10.993832

**VOC headspace analysis, experimental data for March 23rd ,1994.**

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents 1, wastewater, toluene & tag, reactor 2, wastewater, toluene and PCE & tag, reactor 3, wastewater & toluene.

**TOLUENE CONCENTRATION IN REACTOR # 3**

TIME	AREA	CONC	AVERAGE
9	250695	10.262376	
12	187878	8.0857327	7.5867475
12	159077	7.0877623	
16	201940	8.5729887	8.5172706
16	198724	8.4615525	
22	192931	8.2608219	7.7842902
22	165426	7.3077586	
25.5	248717	10.193837	8.7167365
25.5	163460	7.2396356	
35.5	138465	6.3735452	7.1482102
35.5	183178	7.9228751	
40.5	166033	7.3287915	7.4092674
40.5	170678	7.4897433	
50.5	98732	4.996775	3.4409482
50.5	8931	1.8851213	
54	119950	5.7319903	5.3356054
54	97071	4.9392205	
64	52483	3.3942219	3.7214963
64	71373	4.0487707	

**TOLUENE CONCENTRATION IN REACTOR # 2**

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	374652	14.557554	13.936044
0	338779	13.314535	
6	369314	14.372589	13.294559
6	307091	12.216528	

**TOLUENE CONCENTRATION IN REACTOR # 2**

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
9	328650	12.963559	13.072362
9	334930	13.181165	
12	356859	13.941017	13.872755
12	352919	13.804494	
16	289857	11.619361	10.749961
16	239676	9.8805617	
22	258372	10.528388	11.168817
22	295337	11.809246	
25.5	316991	12.559569	12.058695
25.5	288081	11.557821	
35.5	238178	9.8286552	9.8286552
35.5	238178	9.8286552	
40.5	168316	7.4078987	6.8302048
40.5	134972	6.2525109	
50.5	34351	2.7659382	2.5727614
50.5	23201	2.3795846	
54	972	1.6093376	1.6142406
54	1255	1.6191437	
64	0	1.5756572	1.5756572
64	0	1.5756572	



VOC headspace analysis, experimental data for March 23rd, 1994.

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents 1, wastewater, toluene & tag, reactor 2, wastewater, toluene and PCE & tag, reactor 3, wastewater & toluene.

PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	45402	19.4	19.4069	0.00691	0.000048
S2	23174	9.72	9.70386	-0.0161	0.000261
S4	6532	2.43	2.43923	0.00923	0.000085

STDS 0.0001136

Regression Output:

Constant	-0.412143
Std Err of Y Est	0.0198361
R Squared	0.9999973
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 0.0004365  
Std Err of Coef. 0.0000007

PERC CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	36576	15.554151	14.741781
0	32854	13.92941	
6	32406	13.733847	12.540391
6	26938	11.346935	
9	28395	11.98295	11.95283
9	28257	11.92271	
12	28407	11.988188	11.003172
12	23894	10.018156	

PERC CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
16	22942	9.6025858	8.4881405
16	17836	7.3736952	
22	18761	7.7774798	8.6276099
22	22656	9.47774	
25.5	24084	10.101096	9.6409999
25.5	21976	9.1809038	
35.5	20418	8.5007997	8.5007997
35.5	20418	8.5007997	
40.5	18150	7.5107637	6.5386252
40.5	13696	5.5664867	
50.5	18756	7.7752972	6.9734029
50.5	15082	6.1715087	
54	16834	6.9362984	7.7305535
54	20473	8.5248085	
64	17140	7.0698747	6.3454634
64	13821	5.6210522	

**VOC headspace analysis, experimental data for March 23rd ,1994.**

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents 1, wastewater,toluene & tag, reactor 2, wastewater, toluene and PCE & tag, reactor 3, wastewater & toluene.

**PERC CONCENTRATION IN REACTOR # 2**

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	32739	13.87921	14.617808
0	36123	15.356406	
6	31722	13.435265	14.274918
6	35569	15.114572	
9	27646	11.655994	11.292151
9	25979	10.928309	
12	32373	13.719442	12.553705
12	27032	11.387968	
16	23620	9.898549	10.468213
16	26230	11.037876	
22	29548	12.486262	12.793793
22	30957	13.101324	
25.5	33555	14.235413	12.271711
25.5	24558	10.308008	
35.5	28410	11.989498	11.989498
35.5	28410	11.989498	
40.5	26446	11.132165	10.30779
40.5	22669	9.4834148	
50.5	30537	12.917984	12.604997
50.5	29103	12.292009	
54	30848	13.053743	11.260503
54	22632	9.4672634	
64	27137	11.433803	11.374218
64	26864	11.314632	

**REACTOR # 1**

TIME	DO	pH	Temp
hrs	mg/L		°C
0	6.3	7.92	24.1
18	3.8	7.4	23.6
30	4.1	7.04	21.7
64	3.9	6.98	23.3

**REACTOR # 2**

TIME	DO	pH	Temp
hrs	mg/L		°C
0	7.1	7.94	24
18	4.7	7.52	24
30	6	7.37	21.7
64	6.1	7.2	22.3

**REACTOR # 2**

TIME	DO	pH	Temp
hrs	mg/L		°C
0	6.6	7.9	23.6
18	4.7	7.63	23.9
30	3.1	6.94	22.2
64	2.9	6.93	22.1

VOC headspace analysis experimental data for March 29, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 deionized sterile water.

TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	676305	34.34	38.05921	3.719209	13.83252
S2	384398	17.32	21.63208	4.31208	18.59404
S6	223998	8.66	12.60554	3.945536	15.56725
S3	134289	4.33	7.557142	3.227142	10.41445

STDS 3.415443

Regression Output:

Constant	-3.72599
Std Err of Y Est	0.60608
R Squared	0.998637
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s) 5.63E-05

Std Err of Coef. 1.47E-06

TOLUENE CONCENTRATION IN REACTOR #1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	319985	14.28123	14.70468
0	335034	15.12812	
7.5	288429	12.50541	12.19393
7.5	277359	11.88245	
18.5	299585	13.13322	13.57132
18.5	315155	14.00942	
29.5	306019	13.49529	14.49744

TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
29.5	341635	15.49959	
41.5	295554	12.90637	11.63236
41.5	250276	10.35834	
53.5	249751	10.3288	13.27514
53.5	354463	16.22149	
65.5	288556	12.51256	12.37235
65.5	283573	12.23214	
73	332595	14.99086	13.2111
73	269343	11.43134	

TOLUENE CONCENTRATION IN REACTOR 3

Time	AREA	CONC	Average
hrs		mg/L	mg/L
0	296596	12.96501	12.9037
0	294417	12.84239	
7.5	309657	13.70002	10.94414
7.5	211714	8.188259	
18.5	213471	8.287135	9.804286
18.5	267390	11.32144	
29.5	264763	11.1736	12.77694
29.5	321745	14.38028	
41.5	220542	8.685057	8.215609
41.5	203858	7.746161	
53.5	209473	8.062146	9.260189
53.5	252051	10.45823	
65.5	212857	8.252582	7.358706

VOC headspace analysis experimental data for March 29, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 deionized sterile water.

TOLUENE CONCENTRATION IN REACTOR 3

Time hrs	AREA	CONC mg/L	Average mg/L
65.5	181089	6.464831	
73	185831	6.731688	6.783461
73	187671	6.835234	

TOLUENE CONCENTRATION IN REACTOR 2

Time hrs	AREA	CONC mg/L	Average mg/L
0	316388	14.07881	14.65313
0	336799	15.22744	
7.5	268835	11.40276	11.04102
7.5	255979	10.67928	
18.5	344992	15.68851	13.50497
18.5	267390	11.32144	
29.5	276472	11.83253	12.99138
29.5	317657	14.15022	
41.5	317087	14.11815	12.17882
41.5	248164	10.23949	
53.5	275546	11.78042	13.72957
53.5	344818	15.67872	
65.5	315376	14.02186	13.15595
65.5	284602	12.29005	
73	282846	12.19123	10.63201
73	227432	9.072793	

PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	53568	19.4	18.68601	-0.71399	0.509777
S2	30291	9.72	10.46189	0.741892	0.550404
S4	11920	4.86	3.971136	-0.88886	0.79008
S3	30628	9.72	10.58096	0.860959	0.741251

STDS 0.138459

Regression Output:

Constant	-0.24038
Std Err of Y Est	1.138313
R Squared	0.976761
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s) 0.000353  
Std Err of Coef. 3.85E-05

VOC headspace analysis experimental data for March 29, 1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 deionized sterile water.

PERC CONCENTRATION IN REACTOR 3

Time hrs	AREA	CONC mg/L	AVERAGE mg/L
0	28298	9.757734	9.627891
0	27563	9.498048	
7.5	27388	9.436217	7.61682
7.5	17089	5.797423	
18.5	16258	5.503818	6.724875
18.5	23170	7.945933	
29.5	21273	7.275694	8.082313
29.5	25839	8.888932	
41.5	16784	5.689662	5.316384
41.5	14671	4.943106	
53.5	15245	5.145909	5.916667
53.5	19608	6.687424	
65.5	13748	4.616996	5.699378
65.5	19875	6.781759	
73	15660	5.292535	4.948406
73	13712	4.604277	

PERC CONCENTRATION IN REACTOR 1

Time hrs	AREA	CONC mg/L	AVERAGE mg/L
0	32954	11.40277	11.58649
0	33994	11.77022	
7.5	26679	9.185717	9.151269
7.5	26484	9.11682	
18.5	26602	9.158512	9.621708
18.5	29224	10.0849	
29.5	27701	9.546805	10.0683

PERC CONCENTRATION IN REACTOR 1

Time hrs	AREA	CONC mg/L	AVERAGE mg/L
29.5	30653	10.58979	
41.5	25996	8.944402	8.061821
41.5	21000	7.179239	
53.5	30698	10.60569	9.155508
53.5	22489	7.705326	
65.5	23382	8.020836	8.061821
65.5	23614	8.102805	
73	27249	9.387107	8.547983
73	22499	7.708859	

PERC CONCENTRATION IN REACTOR 2

Time hrs	AREA	CONC mg/L	AVERAGE mg/L
0	29401	10.14744	10.67176
0	32369	11.19608	
7.5	23216	7.962186	7.723698
7.5	21866	7.48521	
18.5	29852	10.30679	10.30679
18.5	29852	10.30679	
29.5	23618	8.104219	8.627655
29.5	26581	9.151092	
41.5	26095	8.979381	7.999637
41.5	20549	7.019894	
53.5	22489	7.705326	8.772868
53.5	28532	9.84041	

**VOC headspace analysis experimental data for March 29, 1994.**

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L, reactor contents, 1, 2 & 3 deionized sterile water.

**PERC CONCENTRATION IN REACTOR 2**

Time hrs	AREA	CONC mg/L	AVERAGE mg/L
65.5	25794	8.873033	8.316738
65.5	22645	7.760443	
73	22743	7.795068	6.82822
73	17270	5.861373	

**REACTOR # 3**

TIME hr	DO mg/L	pH	Temp oC
0	6.7	7.51	22.9
18.5	9.2	6.75	21.3
30.5	9.2	6.35	21.8
54.5	10.9	6.93	23.6

**REACTOR # 1**

TIME hr	DO mg/L	pH	Temp oC
0	6.9	7.57	22
8.5	8.9	7.97	21.8
30.5	9.1	7.2	21
54.5	10.1	7.92	23.3

**REACTOR # 2**

TIME hr	DO mg/L	pH	Temp oC
0	6.1	7.44	22.3
18.5	8.8	6.93	21.6
30.5	9.0	6.98	21.2
54.5	9.0	6.92	23.2

# VOC headspace analysis experimental data, April 6, 1994,

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

## PERC CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
35	23041	5.6308751	
44	24251	6.116363	4.186649
44	14632	2.2569351	
47	18132	3.6612388	4.7876911
47	23747	5.9141433	
54.5	22204	5.2950459	3.8088913
54.5	14796	2.3227367	
59	12721	1.4901852	1.5403389
59	12971	1.5904926	
69	18839	3.9449082	2.6128258
69	12199	1.2807433	
74	12157	1.2638917	0.8221379
74	9955	0.380384	
80.5	9323	0.1268069	0.0297093
80.5	8839	-0.067388	
92.5	12821	1.5303082	0.1779637
92.5	6080	-1.174381	
102.5	771	-3.304509	-3.304509
102.5	771	-3.304509	

## REACTOR #1

TIME	DO	pH	TEMP
0	5	7.57	21
18	2.5	7.14	21.8
30	7.1	6.93	23.3
45	2.5	7.04	23.1
50	1.7	6.9	24
74	1.8	6.63	22.5
98	3.3	6.66	23.8
128	2.7	6.59	22.6
152	1.7	6.57	21.4

## REACTOR # 2

TIME	DO	pH	Temp
0	6.2	7.78	21.1
18	7	7.58	20.2
30	3.7	7.37	23.3
45	1.8	7.3	23.6
50	3.5	7.34	23.9
74	3	6.88	23
98	3.8	6.63	23.1
128	3.2	6.28	22.2
152	2.3	6.57	24.2

**VOC headspace analysis experimental data, April 6, 1994,**

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

**REACTOR # 3**

TIME	DO	pH	Temp
0	5.4	7.88	21.9
18	5.1	7.15	21.7
30	4.5	7.22	23
45	5.1	7.24	23.6
50	2.8	7.07	23.2
74	2.7	7.06	22.6
98	3	7.06	22.1
128	2.5	7.02	21.8
152	1.7	6.91	24.3



# VOC headspace analysis experimental data, April 6, 1994,

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	745785	34.34	34.454	0.1139	0.0129723
S2	462873	17.32	21.384	4.0639	16.515135
S6	247135	8.66	11.418	2.7572	7.6020566
S3	91188	4.33	4.2128	-0.1172	0.0137551

STDS 7.84876

### Regression Output:

Constant	-1.70442
Std Err of Y Est	2.5023722
R Squared	0.9762834
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s) 0.0000462  
Std Err of Coef. 0.0000051

## TOLUENE CONCENTRATION IN REACTOR #1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	356491	14.764809	16.24948
0	420765	17.73415	
4.5	351410	14.530076	14.645341
4.5	356400	14.760605	
9	330385	13.55876	13.759399
9	339071	13.960037	

## TOLUENE CONCENTRATION IN REACTOR #1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
18	320463	13.100382	12.558108
18	296987	12.015834	
26	299087	12.11285	12.036346
26	295775	11.959842	
35	258404	10.23337	10.228797
35	258206	10.224223	
44	240392	9.4012489	8.6304787
44	207024	7.8597086	
47	173768	6.3233425	6.917936
47	199509	7.5125294	
54.5	166336	5.9799978	5.4022436
54.5	141324	4.8244894	
59	125944	4.1139616	4.0034094
59	121158	3.8928572	
69	76103	1.8113991	1.6206468
69	67845	1.4298946	
74	474293	20.207045	19.929925
74	462296	19.652806	
80.5	387108	16.179258	17.497454
80.5	444175	18.815649	
92.5	369573	15.369174	14.426731
92.5	328773	13.484289	
102.5	398417	16.701713	16.701713
102.5	398417	16.701713	
105	350655	14.495197	16.301014
105	428832	18.10683	
113	369282	15.35573	15.213694

**VOC headspace analysis experimental data, April 6, 1994,**

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

**TOLUENE CONCENTRATION IN REACTOR #1**

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
113	363133	15.071657	
125	367380	15.267861	15.267861
125	367380	15.267861	
128	332520	13.657393	12.967909
128	302671	12.278424	
147.5	332758	13.668388	14.735681
147.5	378963	15.802974	
151	374959	15.617997	13.970617
151	303641	12.323236	
157.5	345478	14.256029	14.605056
157.5	360588	14.954083	
171.5	370396	15.407195	16.055771
171.5	398474	16.704347	
179.5	363648	15.09545	13.388728
179.5	289761	11.682006	
194.5	313983	12.801018	12.852436
194.5	316209	12.903855	
200.5	333009	13.679984	13.833177
200.5	339641	13.98637	
218.5	320145	13.085691	11.924754
218.5	269886	10.763817	

**TOLUENE CONCENTRATION IN REACTOR # 3**

TIME hrs	AREA	CONC mg/L	Average mg/L
0	381315	15.911632	14.886541
0	336937	13.86145	
4.5	303226	12.304064	13.22156
4.5	342946	14.139055	
9	297183	12.024889	10.140419
9	215601	8.2559502	
18	253897	10.025155	8.6800263
18	195664	7.3348975	
26	309218	12.580884	12.161474
26	291061	11.742064	
35	243556	9.5474199	8.2281158
35	186441	6.9088118	
44	190837	7.111899	6.6717922
44	171784	6.2316854	
47	245713	9.6470693	7.7021729
47	161515	5.7572765	
54.5	185914	6.8844654	7.988486
54.5	233709	9.0925066	
59	220071	8.462456	6.9221862
59	153390	5.3819164	
69	147433	5.1067139	5.1573471
69	149625	5.2079803	
74	507578	21.744751	18.269032
74	357108	14.793314	
80.5	350034	14.466508	13.55779
80.5	310694	12.649072	
92.5	338867	13.950613	13.678205

VOC headspace analysis experimental data, April 6, 1994,

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

TOLUENE CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	Average mg/L
92.5	327074	13.405798	
102.5	326149	13.363065	14.951565
102.5	394918	16.540066	
105	409403	17.209246	16.690071
105	386927	16.170897	
113	273642	10.937338	11.129153
113	281946	11.320967	
125	296501	11.993382	11.431427
125	272173	10.869473	
128	241182	9.4377454	10.572442
128	290305	11.707138	
147.5	232352	9.0298156	9.8856366
147.5	269402	10.741458	
151	261664	10.383976	9.9522312
151	242973	9.5204863	
157.5	295094	11.928381	9.3766714
157.5	184626	6.8249622	
171.5	246911	9.7024147	10.506217
171.5	281709	11.310018	
179.5	349870	14.458931	11.528975
179.5	223027	8.5990178	
194.5	233347	9.0757828	6.5541947
194.5	124183	4.0326067	
200.5	216559	8.3002081	8.3002081
200.5	216559	8.3002081	
218.5	260753	10.34189	9.6385919
218.5	230306	8.9352942	

TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	Average mg/L
0	281700	11.309603	13.65215
0	383113	15.994697	
4.5	344148	14.194585	14.281831
4.5	347925	14.369076	
9	355855	14.735427	14.238497
9	334342	13.741566	
18	294632	11.907037	12.738974
18	330648	13.57091	
26	306604	12.460122	13.31816
26	343750	14.176198	
35	300216	12.165008	12.65547
35	321449	13.145933	
44	248451	9.7735599	10.372427
44	274377	10.971293	
47	253369	10.000762	8.9067899
47	206009	7.8128175	
54.5	256125	10.128085	9.8305915
54.5	243246	9.5330984	
59	295846	11.963122	10.187195
59	218963	8.4112685	
69	185817	6.8799842	7.2195407
69	200517	7.5590972	
74	527120	22.647555	19.656432
74	397629	16.665309	
80.5	391429	16.378881	16.714418
80.5	405955	17.049955	
92.5	474591	20.220812	17.835093

# VOC headspace analysis experimental data, April 6, 1994,

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	Average mg/L
92.5	371309	15.449374	
102.5	424234	17.894411	16.149969
102.5	348714	14.405526	
105	414355	17.43802	17.106479
105	400002	16.774937	
113	310975	12.662054	14.111082
113	373706	15.560111	
125	344731	14.221519	12.32289
125	262536	10.424261	
128	284029	11.417198	12.341415
128	324040	13.265633	
147.5	262315	10.414051	11.258554
147.5	298875	12.103056	
151	290141	11.699561	11.915538
151	299491	12.131514	
157.5	334396	13.744061	12.55
157.5	282703	11.355939	
171.5	219817	8.4507217	7.6067737
171.5	183281	6.7628256	
179.5	210067	8.0002896	7.694504
179.5	196829	7.3887183	
194.5	138548	4.6962433	5.0727121
194.5	154846	5.4491809	
200.5	162023	5.7807451	5.9404522
200.5	168937	6.1001592	
218.5	105627	3.1753536	3.1219716
218.5	103316	3.0685896	

## PERCHLOROETHYLENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	55937	19.4	18.830	-0.5703	0.325213
S2	34921	9.72	10.398	0.67748	0.4589837
S4	19213	4.86	4.0950	-0.7650	0.5852739
S3	34872	9.72	10.378	0.65782	0.4327312
				STDS	0.1068465

## Regression Output:

Constant	-3.613857
Std Err of Y Est	0.9492633
R Squared	0.9838388
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.0004012
Std Err of Coef.	0.0000364

# VOC headspace analysis experimental data, April 6, 1994,

Initial reactor concentration of toluene 9.6 mg/L and PCE 5.3 mg/L. reactors all contain wastewater, reactor 1 toluene, tag & scrapings, reactor 2 toluene, PCE, tag and scrapings, reactor 3 toluene and PCE.

## PERC CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	26813	7.1443134	9.6710571
0	39408	12.197801	
4.5	32831	9.5589134	9.5759656
4.5	32916	9.5930179	
9	31787	9.1400296	8.8545547
9	30364	8.5690798	
18	24580	6.2483676	7.0690828
18	28671	7.889798	
26	25709	6.7013558	7.2598675
26	28493	7.8183792	
35	24358	6.1592946	6.6377609
35	26743	7.1162273	
44	20396	4.5696227	5.1002489
44	23041	5.6308751	
47	21227	4.9030446	3.9475162
47	16464	2.9919878	
54.5	21976	5.2035656	4.9275196
54.5	20600	4.6514736	
59	16549	3.0260923	3.6483995
59	19651	4.2707067	
69	17961	3.5926286	4.1284707
69	20632	4.6643129	
74	20376	4.5615981	3.4018439
74	14595	2.2420896	
80.5	14533	2.2172133	2.3630603
80.5	15260	2.5089073	
92.5	18860	3.953334	2.9799509

## PERC CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
92.5	14008	2.0065678	
102.5	16742	3.1035296	2.3169189
102.5	12821	1.5303082	
105	16545	3.0244874	2.9233775
105	16041	2.8222676	
113	12090	1.2370093	1.8454741
113	15123	2.4539388	
125	14332	2.1365662	1.2482437
125	9904	0.3599213	
128	11688	1.075715	1.533518
128	13970	1.991321	

## PERC CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	41364	12.982606	11.702884
0	34985	10.423162	
4.5	28751	7.9218964	10.137487
4.5	39795	12.353077	
9	27681	7.4925807	6.1131532
9	20805	4.7337257	
18	31988	9.2206768	8.1987449
18	26894	7.176813	
26	22319	5.3411873	4.0500304
26	15883	2.7588734	
35	18831	3.9416983	4.7862867

# VOC headspace analysis, experimental data for April 19th ,1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L., reactors all contain wastewater, reactors 1 & 2 toluene, tag, scrapings, reactor 3 toluene.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	765766	34.34	35.134	0.79365	0.6299
S2	354897	17.32	16.283	-1.0372	1.0758
S6	210813	8.66	9.6722	1.01218	1.0245
S3	109692	4.33	5.0327	0.70271	0.4938

STDS 0.2881

## Regression Output:

Constant	-0.367841
Std Err of Y Est	1.1581723
R Squared	0.9949196
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s) 0.0000459  
Std Err of Coef. 0.0000023

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	363397	16.6728	16.6728
0	356045	16.6728	
5	287306	13.181714	13.181714
5	245064	13.181714	
17	276933	12.705797	12.705797

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
17	248812	12.705797	
24	205792	9.4418193	9.4418193
24	256978	9.4418193	
32	240585	11.038136	11.038136
32	216575	11.038136	
45	204612	9.3876804	9.3876804
45	195589	9.3876804	
48.5	218161	10.009314	10.009314
48.5	208312	10.009314	
54	183156	8.4032705	8.4032705
54	128956	8.4032705	
66	142980	6.5599796	6.5599796
66	130567	6.5599796	
78	126022	5.7819398	5.7819398
78	114674	5.7819398	
91	113412	5.2033879	5.2033879
91	108939	5.2033879	

## TOLUENE CONCENTRATION IN REACTOR # 3

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	305383	14.011094	12.636563
0	245465	11.262032	
5	303468	13.923233	11.609921
5	202627	9.2966078	

VOC headspace analysis, experimental data for April 19th ,1994.

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L., reactors all contain wastewater, reactors 1 & 2 toluene, tag, scrapings, reactor 3 toluene.

TOLUENE CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
17	269914	12.383762	10.953418
17	207563	9.5230735	
24	245629	11.269557	10.421825
24	208675	9.5740925	
32	235734	10.81557	10.153126
32	206857	9.4906819	
45	70530	3.2359446	3.6451978
45	88370	4.0544509	
48.5	53889	2.4724489	2.1919591
48.5	41662	1.9114692	
54	12442	0.5708439	0.5327861
54	10783	0.4947284	
66	7524	0.3452041	0.3886758
66	9419	0.4321475	
78	7605	0.3489204	0.334124
78	6960	0.3193276	
91	6352	0.2914323	0.2914323

TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
17	265249	12.16973	
24	201945	9.2653174	9.8324909
24	226669	10.399664	
32	215468	9.885758	9.3856158
32	193666	8.8854735	
45	203649	9.3434976	9.0499089
45	190851	8.7563202	
48.5	204227	9.3700165	8.6629536
48.5	173405	7.9558908	
54	190593	8.7444831	8.5415311
54	181746	8.3385792	
66	209690	9.6206611	8.9250454
66	179367	8.2294297	
78	192727	8.8423919	8.6408622
78	183942	8.4393325	
91	236654	10.85778	9.7246031
91	187257	8.5914261	

TOLUENE CONCENTRATION IN REACTOR # 2

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	297444	13.64685	14.671267
0	342100	15.695685	
5	234363	10.752668	10.214399
5	210899	9.6761305	
17	218476	10.023766	11.096748

**VOC headspace analysis, experimental data for April 19th ,1994.**

Initial reactor concentration for toluene 9.6 mg/L and PCE 5.3 mg/L., reactors all contain wastewater, reactors 1 & 2 toluene, tag, scrapings, reactor 3 toluene.

**REACTOR # 1**

TIME hrs	DO mg/L	pH	Temp °C
0	5	7.57	21
18	2.5	7.14	21.8
30	7.1	6.93	23.3
45	2.5	7.04	23.1
50	1.7	6.9	24
74	1.8	6.63	22.5
98	3.3	6.66	23.8
128	2.7	6.59	22.6
152	1.7	6.57	21.4

**REACTOR # 2**

TIME hrs	DO mg/L	pH	Temp °C
0	6.2	7.78	21.1
18	7	7.58	20.2
30	3.7	7.37	23.3
45	1.8	7.3	23.6
50	3.5	7.34	23.9
74	3	6.88	23
98	3.8	6.63	23.1
128	3.2	6.28	22.2
152	2.3	6.57	24.2

**REACTOR # 3**

TIME hrs	DO mg/L	pH	Temp °C
0	5.4	7.88	21.9
18	5.1	7.15	21.7
30	4.5	7.22	23
45	5.1	7.24	23.6
50	2.8	7.07	23.2
74	2.7	7.06	22.6
98	3	7.06	22.1
128	2.5	7.02	21.8
152	1.7	6.91	24.3



# VOC headspace analysis experimental data,for April 25th, 1994.

Initial reactor concentration for toluene 9.6 mg/L.,reactors all contain wastewater, reactor 1 & 2 toluene, tag & scrapings, reactor 3 toluene

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	765766	34.34	35.134	0.79365	0.62988
S2	354897	17.32	16.283	-1.0372	1.07575
S6	210813	8.66	9.6722	1.01218	1.02452
S3	109692	4.33	5.0327	0.70271	0.49381
STDS				0.2880964	

### Regression Output:

Constant	-0.367841
Std Err of Y Est	1.1581723
R Squared	0.9949196
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.0000459
Std Err of Coef.	0.0000023

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	273292	12.170905	12.345824
0	280917	12.520743	
7	235869	10.453923	10.065224
7	218925	9.6765255	
14.5	186099	8.1704555	8.3372078
14.5	193368	8.5039601	
20.5	171601	7.5052814	7.7015807

## TOLUENE CONCENTRATION IN REACTOR # 1

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
20.5	180158	7.89788	
33.5	155504	6.7667446	6.3156944
33.5	135842	5.8646442	
39.5	132309	5.7025488	6.0769558
39.5	148630	6.4513628	
49.5	134051	5.7824724	5.9269957
49.5	140351	6.0715189	

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME	AREA	CONC	AVERAGE
hrs		mg/L	mg/L
0	189563	8.3293852	9.4390715
0	237936	10.548758	
7	188470	8.2792379	8.2792379
7	188470	8.2792379	
14.5	294524	13.145038	12.285767
14.5	257067	11.426496	
20.5	284057	12.664808	10.421761
20.5	186279	8.178714	
33.5	135514	5.8495954	4.765281
33.5	88247	3.6809666	
39.5	71630	2.918572	2.918572
39.5	71630	2.918572	
49.5	74022	3.0283179	2.9536934
49.5	70769	2.879069	

# VOC headspace analysis experimental data,for April 25th, 1994.

Initial reactor concentration for toluene 9.6 mg/L.,reactors all contain wastewater, reactor 1 & 2 toluene, tag & scrapings, reactor 3 toluene

## TOLUENE CONCENTRATION IN REACTOR # 3

TIME hrs	AREA	CONC mg/L	AVERAGE mg/L
0	256858	11.416907	11.499973
0	260479	11.58304	
7	235613	10.442178	9.2438963
7	183378	8.0456149	
14.5	255876	11.371852	12.303408
14.5	296484	13.234963	
20.5	226187	10.009709	9.3082435
20.5	195609	8.6067781	
33.5	227388	10.064811	9.5754969
33.5	206058	9.0861824	
39.5	235463	10.435296	10.551671
39.5	240536	10.668047	
49.5	249127	11.062205	9.8327253
49.5	195532	8.6032453	

## REACTOR # 1

TIME	DO	pH	Temp
0	5	7.57	21
18	2.5	7.14	21.8
30	7.1	6.93	23.3
49	2.5	7.04	23.1

## REACTOR # 2

TIME	DO	pH	Temp
0	6.2	7.78	21.1
7	7	7.58	20.2
14.5	3.7	7.37	23.3
20	1.8	7.3	23.6
33	3.5	7.34	23.9
49	3	6.88	23

## REACTOR # 3

TIME	DO	pH	Temp
0	5.4	7.88	21.9
7	5.1	7.15	21.7
14.5	4.5	7.22	23
20	5.1	7.24	23.6
33	2.8	7.07	23.2
49	2.7	7.06	22.6

# VOC headspace analysis experimental data, for May 10th, 1994.

Initial concentration of toluene 9.3 mg/L., reactor content wastewater & toluene.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Stand	AREA	CONC	FIT	ERR	ERR2
S1	647987	34.34	37.08552	2.745524	7.5379
S6	202636	8.66	11.59724	2.937242	8.627392
S#	196080	8.66	11.22203	2.56203	6.563997

STDS 1.032237

## Regression Output:

Constant	-2.74827
Std Err of Y Est	0.265336
R Squared	0.99984
No. of Observations	3
Degrees of Freedom	1

X Coefficient(s) 5.72E-05.  
Std Err of Coef. 7.24E-07

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME	AREA	CONC	Average
hrs	mg/L	mg/L	
0	241103	11.05052	11.3717
0	252327	11.69289	
12	177421	7.405875	9.192998
12	239873	10.98012	
18	219857	9.834567	8.832151
18	184827	7.829734	
26	224838	10.11964	9.590903
26	206361	9.062166	

## TOLUENE CONCENTRATION IN REACTOR # 2

TIME	AREA	CONC	Average
hrs	mg/L	mg/L	
34.5	152188	5.961742	6.608978
34.5	174806	7.256213	
52.5	113801	3.764782	2.89211
52.5	83305	2.019438	
76.5	50505	0.142232	1.011241
76.5	80873	1.88025	

## REACTOR # 2

TIME	DO	pH	Temp
0	6.2	7.78	21.1
6	3.7	7.37	23.3
12	1.8	7.3	23.6
18	3.5	7.34	23.9
26	3	6.88	23
34.5	3.8	6.63	23.1
52.5	3.2	6.28	22.2
76.5	2.3	6.57	24.2

# VOC headspace analysis experimental data,for May 18th, 1994.

Initial concentration of toluene 9.3 mg/L., reactor content deionized water, toluene, tage and scrapings.

## TOLUENE STANDARDS FOR EXPERIMENTAL SAMPLES

Standard	AREA	CONC	FIT	ERR	ERR2
S1	647125	34.34	35.12425	0.784247	0.615044
S2	334447	17.32	18.15291	0.832906	0.693732
S6	159943	8.66	8.681286	0.021286	0.000453
S3	104622	4.33	5.678608	1.348608	1.818743

STDS 0.757478

### Regression Output:

Constant	-0.74676
Std Err of Y Est	0.669835
R Squared	0.998301
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s) 5.43E-05  
Std Err of Coef. 1.58E-06

## TOLUENE CONCENTRATION IN REACTOR 1

Time hrs	AREA	CONC mg/L	Average mg/L
16	271433	13.98591	
21.5	236089	12.06753	10.76582
21.5	188124	9.464115	
32	197378	9.966398	10.35709
32	211774	10.74778	
52	435190	22.87421	21.95437
52	401296	21.03453	
68	396827	20.79197	19.84181
68	361816	18.89166	
87	390792	20.4644	19.22216
87	345018	17.97991	
99	366375	19.13911	17.79276
99	316765	16.44641	
109	339345	17.67199	16.82738
109	308223	15.98277	
133	285784	14.76484	14.88349
133	290156	15.00214	

## TOLUENE CONCENTRATION IN REACTOR 1

Time hrs	AREA	CONC mg/L	Average mg/L
0	288575	14.91633	15.08503
0	294791	15.25372	
6	297951	15.42524	15.27733
6	292501	15.12943	
16	302817	15.68935	14.83763

# **Fate of Volatile Organic Compounds in Wastewater Collection Systems**

## **Volume V: Gas-Liquid Mass Transfer at Drop Structures**

Conference Papers

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

September, 1994

## 6. ADDITIONAL RESEARCH

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As described in Section 1.3, funding from the Natural Science and Engineering Research Council (NSERC) as well as Environment Canada made it possible to complete research which is of direct relevance to this study. In particular, pilot experiments were completed in order to study gas-liquid mass transfer of VOCs at sewer drop structures, and laboratory experiments were completed to determine the potential for pre- and post-discharge formation of chloroform resulting from the use of hypochlorite-containing bleaches. Brief descriptions of each study are provided below, with an emphasis on major conclusions. The reader is referred to Volumes V, VI, and VII of this report for details regarding previous research, experimental methodologies, and collective results.

### 6.1 GAS-LIQUID MASS TRANSFER AT DROP STRUCTURES

A pilot drop structure was constructed and maintained at the Wastewater Technology Centre in Burlington, Ontario. The system was designed for flexibility, and allowed for variations in water flowrate, headspace ventilation rate, drop height, tailwater depth, and VOC physicochemical properties. The latter were varied through the introduction of a multi-tracer "cocktail" during each experiment. Tracer stripping efficiencies and mass transfer coefficients were determined over a wide range of system operating conditions. The reader is referred to Volume V for specific details regarding experimental methodologies and results. Several important conclusions are provided below.

1. At drop structures, stripping efficiencies for VOCs is a complex function of many system operating conditions. Therefore, emissions estimates based on simple stripping or emission factors are likely characterized by significant uncertainty.
2. Stripping efficiencies and mass transfer coefficients for VOCs at sewer drop structures are a strong function of compound physicochemical properties,

particularly Henry's law coefficient. This suggests the potential importance of air entrainment as a mass transfer mechanism.

3. Ratios of gas- to liquid-phase mass transfer coefficients for some sewer drop structures are much lower than those reported for other water and wastewater treatment processes.
4. Stripping efficiencies are significantly affected by the finite ventilation conditions associated with many sewer atmospheres, and attempts to model emissions from sewer drop structures using open (infinite) ventilation conditions can lead to significant overestimates of such emissions.
5. Stripping efficiencies are significantly affected by hydraulic residence time in tailwater pools at the bottom of drop structures. This may be true even when the magnitude of system mass transfer coefficients and/or air entrainment rates are reduced for low water flowrates. This conclusion is most relevant at locations characterized by well-defined tailwater pools, e.g., pump station wet wells.
6. Existing models to estimate oxygen transfer at weirs and other drop structures are not appropriate for use in estimating VOC emissions from drop structures characterized by an accumulation of tailwater.
7. Drop structures are likely to be the dominant source of gas-liquid mass transfer in municipal sewers.

## **6.2 FORMATION OF CHLOROFORM**

As noted in Section 2.2, one of the target VOCs (chloroform) can form when free residual chlorine reacts with appropriate organic precursors. Chloroform formation in drinking water and treated wastewater has been extensively studied. Two novel studies were completed in the School of Engineering at the University of Guelph. The first involved an assessment of chloroform formation in residential washing machines, following the introduction of bleaches containing sodium hypochlorite. These studies were

completed in a commercial washing machine, and demonstrated a high potential for chloroform formation under appropriate machine operating conditions. On average, 15% of the chloroform formed during a wash cycle was emitted to indoor air. The remainder is discharged to municipal sewers, along with any free residual chlorine remaining in wash water. The second study involved the determination of chloroform formation factors associated with free residual chlorine discharges to raw (untreated) municipal wastewater. The reader is referred to Volumes VI and VII for detailed descriptions of experimental methodologies and results associated with chloroform formation studies. Several important conclusions stemming from those studies are listed below.

1. Laundry wash water contains surrogates necessary for the formation of chloroform.
2. Chlorine reacts quickly in washing machines, in part to form chloroform.
3. Significant levels of chloroform (upwards of 1.5 mg/L) can be generated following the addition of bleach to wash water.
4. During wash cycles, the gas-liquid mass transfer process associated with chloroform transfer from wash water to headspace does not approach equilibrium.
5. Chloroform stripping efficiencies from washing machines far exceed those previously reported for the less-volatile compound ethanol. However, for this study the average chloroform stripping efficiency of 15% was significantly lower than those reported previously based on radon transfer. Thus, approximately 85% of the chloroform which enters and forms within washing machines is ultimately discharged to municipal sewers.
6. On a unit activity basis, chloroform emissions from washing machines into which chlorinated bleach has been added far exceed chloroform emissions from a showering activity.



7. Chloroform formation in sewers is significantly affected by wastewater characteristics. Specifically, chloroform formation is inversely related to total and volatile suspended solids concentrations, and reaches a peak near pH 8.3.
8. Chloroform yield coefficients ( $\mu\text{g}$  of chloroform formed per mg of  $\text{Cl}_2$  added) were similar for washing machine wash water and untreated wastewater (approximately 0.5 to 5  $\mu\text{g}/\text{mg}$ ). However, the higher free residual chlorine levels observed in washing machines suggest that they dominate in-situ (in sewer) formation of chloroform.
9. For cities that use primarily groundwater as their drinking water supply, washing machines may be the primary source of chloroform discharges to municipal sewers.

93-WA-72A.04

## VOC Emissions from Small Sewer Drop Structures

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A S S O C I A T I O N

◆  
SINCE 1907

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## INTRODUCTION

Relative to other organic contaminants, volatile organic compounds (VOCs) have an affinity for the gas phase. They are generally characterized as having lower boiling points, e.g. less than 100 °C at 1 atmosphere, and higher gas-liquid partition coefficients (Henry's law coefficients), e.g. greater than  $1 \times 10^{-3}$  atm·m<sup>3</sup>/mole at 20 °C, than other organic contaminants. Many VOCs are classified as reactive organic gases (ROGs) that contribute to the generation of ozone in urban airsheds. Others, e.g. 1,1,1-trichloroethane, are relatively inert in the troposphere, but act similar to chlorofluorocarbons in depleting stratospheric ozone. Finally, many VOCs are considered to be toxic air contaminants (TAC), e.g. benzene and vinyl chloride, which at high concentrations may pose acute health risks and at low concentrations may pose chronic, mutagenic health hazards. Because of the many concerns related to VOCs, there has been increasing interest in their fate and control in both natural and engineered systems.

In the United States, the new Clean Air Act and many more stringent state regulations have placed increased regulatory scrutiny on non-conventional sources of VOCs, including municipal wastewater collection and treatment systems and on-site industrial sewers and treatment processes. Thus, in the past three years there has been a significant amount of research associated with VOC emissions from wastewater.<sup>1-6</sup> However, past research has focussed on secondary wastewater treatment facilities. The question of whether VOC loadings in the influent streams to wastewater treatment plants constitute a large or small fraction of total VOC discharges to upstream sewers has not been addressed.

Studies which have focussed on VOC emissions from sewers have indicated that, with some exceptions, relative removal by stripping along 1 to 5 km stretches of relatively uniform sewer channels are small, i.e. less than 10%.<sup>7</sup> However, there is little information to suggest the relative importance of VOC emissions from small sewer drop structures, e.g. drops into pump station wet wells or drop manholes. The research described in this paper begins to address the issue of VOC emissions from sewer drop structures, and suggests the importance of system operating conditions and chemical properties on stripping efficiencies from such systems.

## BACKGROUND

Gas-liquid mass transfer of VOCs and semi-VOCs can be classified as occurring at two general locations in WCS: 1) along relatively-uniform flowing sewer reaches, e.g. interceptor channels, and 2) at points of rapid dissipation of potential energy, e.g. drop manholes or free-fall drops into pump station wet wells.<sup>8,9</sup> In either case, the rate of gas-liquid mass transfer between wastewater and a sewer atmosphere can be represented mathematically as

$$R_v = -K_L \left( C - \frac{C_g}{H_c} \right) A, \quad (1)$$

where

- $R_v$  = mass transfer rate across wastewater-air interface (mg/hr)
- $K_L$  = overall mass transfer coefficient (m/hr)
- $C$  = concentration of contaminant in the liquid phase (mg/m<sup>3</sup>)
- $C_g$  = concentration of contaminant in the gas phase (mg/m<sup>3</sup>)
- $H_c$  = compound-specific Henry's law coefficient ((mg/m<sup>3</sup>)<sub>gas</sub>/[(mg/m<sup>3</sup>)<sub>liq</sub>])
- $A$  = area of wastewater-air interface (m<sup>2</sup>).

According to two-film theory, the inverse of the overall mass transfer coefficient can be written in terms of liquid- and gas-phase mass transfer resistances such that

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \quad (2)$$

where

- $k_l$  = liquid-phase mass transfer coefficient (m/hr)  
 $k_g$  = gas-phase mass transfer coefficient (m/hr).

Several mechanisms can contribute to gas-liquid mass transfer at sewer drop structures. Mass transfer can occur at

- the free-falling wastewater surface,
- splashing and airborne droplets generated at the tailwater surface,
- agitated tailwater surface, and
- air bubbles entrained in the tailwater.

However, experimental separation of mechanisms a-d is complex at best, and methods to predict the contribution of each mechanism have not been reported. For these reasons, existing models of mass transfer at drop structures are highly empirical.<sup>5,10-12</sup> General extrapolation of these models is characterized by a high degree of uncertainty.

#### Lumped Mechanism Model

A lumped mechanism model (LMM) for mass transfer at drop structures is based upon application of Equation 1, with an assumption that overall mass transfer can be "lumped" into a single "system" mass transfer coefficient  $K_L$ . This is analogous to applications for surface aerators, in which mass transfer caused by entrained air, airborne droplets and surface agitation are effectively accounted for using a single mass transfer coefficient. In such systems,  $K_L a$  values are obtained by dividing the product  $K_L A$  by reactor volume  $V$  ( $a = A/V$ ) and solving for  $K_L a$  directly using data from batch reactor oxygen transfer experiments. However, like surface aerators,  $K_L a$  (oxygen) or  $K_L a$  (VOC) values for drop structures are system-specific and highly dependant on both system geometry and localized non-uniformities in interfacial contact area. Nevertheless, there may be utility in LMM if easily obtainable  $K_L a$  (oxygen) values can be theoretically related or empirically correlated to values of  $k_l a$  (VOC).

If it is assumed that mass transfer to/from a falling wastewater is negligible compared to stripping caused by entrained air and splashing in the tailwater,  $C$  in Equation 1 is replaced by the downstream concentration  $C_2$ . Steady-state mass balances on the gas and liquid phases of an enclosed drop structure then yield

$$\text{Liquid: } Q C_1 - Q C_2 - K_L \left( C_2 - \frac{C_g}{H_c} \right) A = 0, \quad (3)$$

and

$$\text{Gas: } Q_g C_{g,i} - Q_g C_g + K_L \left( C_2 - \frac{C_g}{H_c} \right) A = 0, \quad (4)$$

where

- $C_1$  = contaminant concentration in wastewater at the top of a drop (mg/m<sup>3</sup>)  
 $C_2$  = contaminant concentration in tailwater (mg/m<sup>3</sup>)  
 $C_g$  = contaminant concentration in drop structure headspace (mg/m<sup>3</sup>)

- $A$  = interfacial contact area between wastewater and headspace ( $m^2$ )  
 $C_{g,i}$  = influent gaseous contaminant concentration ( $mg/m^3$ )  
 $Q$  = liquid flowrate ( $m^3/hr$ )  
 $Q_g$  = headspace ventilation rate ( $m^3/hr$ )  
 $K_L$  = overall system mass transfer coefficient ( $m/hr$ ).

By dividing by liquid volume and making the simplifying assumption that  $C_{g,i} \ll C_g$ , Equations 3 and 4 can be rewritten as

$$\frac{1}{\theta_H} C_1 - \frac{1}{\theta_H} C_2 - K_L a \left( C_2 - \frac{C_g}{H_c} \right) = 0 \quad (5)$$

$$- \frac{Q_g}{V_l} C_g + K_L a \left( C_2 - \frac{C_g}{H_c} \right) = 0 \quad (6)$$

where

- $\theta_H$  = hydraulic residence time (HRT) in the tailwater (hr)  
 $a$  = specific area =  $A/V$  ( $1/m$ )  
 $V$  = tailwater volume ( $m^3$ )

Solution of Equations 5 and 6 simultaneously leads to

$$\frac{C_2}{C_1} = \frac{1}{(1 + K_L a \theta_H f)} \quad (7)$$

where  $f$  is a factor that accounts for finite ventilation of the drop structure headspace and is equal to

$$f = \left\{ 1 - \frac{1}{\frac{Q_g H_c}{V K_L a} + 1} \right\} \quad (8)$$

Equation 8 indicates that an infinite ventilation condition can be approached, or reasonably assumed, if the product of  $Q_g H_c$  is large, or  $V K_L a$  is small.

The value of  $(1 - C_2/C_1)$  is a measure of the amount of contaminant lost from wastewater by stripping at a drop structure, and can be estimated if liquid flowrate, tailwater volume, headspace ventilation rate, Henry's law coefficient, and  $K_L a$  are known or reasonably estimated. For most applications, an accurate value for the variable  $K_L a$  will be the limiting factor to applying Equation 7.

Equations 5 and 6 can be used to estimate contaminant accumulation in the headspace of a drop structure. Solving these equations for  $C_g$  yields

$$C_g = \frac{C_2}{\frac{Q_g}{V K_L a} + \frac{1}{H_c}} \quad (9)$$

Equations 5 and 6 can be used to estimate  $K_L a$  based on measurable variables from field or pilot experiments such that

$$K_{La} = \frac{C_1 - C_2}{\theta_H \left\{ C_2 - \frac{C_g}{H_c} \right\}} \quad (10)$$

or

$$K_{La} = \frac{Q_g C_g}{\left\{ C_2 - \frac{C_g}{H_c} \right\} V} \quad (11)$$

Field measurements or controlled tracer introduction allows knowledge of  $C_1$ ,  $C_2$ , and  $C_g$ . Values of  $V$  and  $Q_g$  can be easily measured or controlled, and  $H_c$  can be estimated from the literature if wastewater temperature is known.<sup>13</sup> Thus, application of Equations 10 or 11 allows estimates of system-specific mass transfer coefficients.

Equation 2 can be solved for the ratio of liquid-to-gas phase mass transfer coefficients at a drop structure such that

$$\frac{k_{ja}}{k_{ga}} = \frac{k_l}{k_g} = \left\{ \frac{k_{ja}}{K_{La}} - 1 \right\} H_c \quad (12)$$

Thus,  $K_{La}$  obtained from Equation 10 or 11 can be coupled with estimates of  $k_{ja}$  to assess the magnitude of  $k_{ga}$  and relative significance of gas-phase mass transfer resistance for various drop structure operating conditions.

Values of  $k_{ja}$  for two compounds can be related according to their liquid-phase molecular diffusion coefficients ( $D_l$ ) by

$$\frac{k_{ja} \text{ (compound i)}}{k_{ja} \text{ (compound j)}} = \left\{ \frac{D_l \text{ (compound i)}}{D_l \text{ (compound j)}} \right\}^n = \psi \quad (13)$$

where  $n$  varies from 0.5 to 1.0 according to penetration and two-film theories, respectively. If compound  $j$  is a very volatile compound (high  $H_c$ ),  $k_{ja}$  (compound  $j$ ) can be reasonably estimated as  $K_{La}$  (compound  $j$ ) using Equation 10 or 11. Thus, if measurements of a highly volatile chemical  $j$  are made upstream and downstream of a drop structure, it should be possible to estimate  $k_{ja}$  (compound  $i$ ) using Equation 13, where  $i$  can be any organic contaminant. Independent estimates of  $K_{La}$  for contaminant  $i$  then allow an estimate of the importance of gas-phase resistance through the use of Equations 2 and 12.

### Entrainment Dominated Model

Entrainment dominated models (EDM) are based on the assumption that mass transfer at drop structures is due entirely to air bubbles entrained in tailwater. Thus, steady-state mass balances on the well-mixed tailwater and headspace of an enclosed drop structure lead to

$$\text{Liquid: } QC_1 - QC_2 - Q_e \gamma (C_2 H_c - C_g) = 0 \quad (14)$$

$$\text{Gas: } Q_g C_{g,i} - Q_g C_g + Q_e \gamma (C_2 H_c - C_g) = 0 \quad (15)$$

where

$Q_e$  = rate of air entrainment into tailwater ( $m^3/hr$ )

$\gamma$  = degree of saturation of air bubbles exiting a tailwater surface (-).

All other variables are as described previously. Here,  $\gamma$  can take on values ranging from 0 to 1.

By dividing Equations 14 and 15 by  $V$  and assuming  $C_{g,i} \ll C_g$ , the following two equations result:

$$\frac{1}{\theta_H} C_1 - \frac{1}{\theta_H} C_2 - \frac{Q_e \gamma}{V} (C_2 H_c - C_g) = 0 \quad (16)$$

$$- \frac{Q_g}{V} C_g + \frac{Q_e \gamma}{V} (C_2 H_c - C_g) = 0 \quad (17)$$

Simultaneous solution of Equations 16 and 17 leads to

$$\frac{C_2}{C_1} = \frac{1}{\left\{ 1 + \frac{Q_e \gamma H_c}{Q} \left[ 1 - \frac{1}{1 + \frac{Q_g}{Q_e \gamma}} \right] \right\}} \quad (18)$$

Equation 18 indicates the significance of entrained air bubbles in tailwater, liquid flowrate into a drop structure, and headspace ventilation rate. The denominator includes the ratio  $Q_e/Q$ . As this ratio becomes very large, i.e. large surface area associated with significant air entrainment and/or long HRT in tailwater, contaminant stripping from the drop system can be very high. The bracketed term within the denominator accounts for finite ventilation conditions, and entrainment of partially-contaminated bubbles into a tailwater. If  $Q_e$  is held constant, the bracketed term approaches unity (infinite ventilation) as  $Q_g$  increases. Otherwise, the term is less than unity leading to smaller values of  $C_2/C_1$ . For such conditions there is a retardation of mass transfer, and subsequent reduction in emissions, caused by gaseous accumulation in the drop structure headspace.

Equations 16 and 17 can also be used to estimate contaminant accumulation in the headspace of a drop structure. Solving these Equations for  $C_g$  yields

$$C_g = \frac{C_2}{\frac{1}{H_c} \left\{ 1 + \frac{Q_g}{Q_e \gamma} \right\}} \quad (19)$$

As  $Q_g/Q_e$  becomes very small, an equilibrium condition is approached and  $C_g$  can be reasonably estimated using Henry's law, i.e.  $C_g = C_2 H_c$ .

Equations 16 and 17 can be used to estimate  $Q_e$  based on measured contaminant concentrations in the liquid and gas phases such that

$$Q_e = \frac{Q (C_1 - C_2)}{\gamma (C_2 H_c - C_g)} \quad (20)$$

$$Q_e = \frac{Q_g C_g}{\gamma (C_2 H_c - C_g)} \quad (21)$$

The major limitation to using Equations 20 and 21 to estimate  $Q_e$  is a lack of published information or methodology for estimating the degree of saturation term  $\gamma$ . It is conceivable that this value could be close to unity for contaminants with very low values of  $H_c$ , since only a small mass is then required in a rising bubble before it reaches saturation. Roberts *et al.*<sup>14</sup> provided a mathematical expression to estimate the degree of saturation of rising air bubbles in

a conventional diffused bubble aeration system, given some simplifying assumptions, e.g. constant bubble diameter. However, the associated boundary conditions and simplifying assumptions may not be valid for air entrainment in a drop structure tailwater.

## METHODOLOGY

A pilot-scale drop structure was constructed at the Wastewater Technology Centre (WTC) in Burlington, Ontario. An illustration of the entire experimental system is provided in Figure 1. The system consisted of five major components: water supply system, tracer injection system, enclosed drop chamber, headspace ventilation system, and sample collection system. Each of these components is described below.

Three possible water supplies were available to the experimental system. These included: 1) raw, degrittied wastewater, 2) direct tap water and 3) temperature-regulated tap supplied from a large storage tank. For this study, only direct tap water was used. Water flowrate was controlled using a magnetic flow meter and pneumatic controller.

Volatile tracers were stored in a 25 l collapsible Tedlar bag, which had the advantages of being inert to many volatile tracers, and the ability to maintain a zero headspace during experiments. Tracers were pumped from the bag using a peristaltic pump and 6 mm i.d. Teflon transport tubing. The tracer solution was injected immediately upstream of a static mixer through a 6 mm i.d. stainless-steel tube extending into the pressurized water supply. Following the static mixer, the water/tracer solution was pumped to an enclosed gravity-flow entrance pipe (PVC) connected to the drop chamber.

A schematic of the pilot drop chamber is provided in Figure 2. The chamber consisted of a cylindrical, fibreglass tank with a height of 3.0 m and an internal diameter of 1.5 m. Water flowed into the chamber, flowed over a drop, and accumulated in the base (tailwater) of the chamber before exiting to a floor drain. Tailwater depth was controlled through vertical adjustments of a flexible hose attached to the effluent pipe. Three flanges of 15 cm i.d. were staggered around the perimeter of the chamber at heights of 1.2 m, 1.8 m, and 2.5 m, measured as the distance from an entry pipe invert to the chamber floor. A fourth flanged entry of 30 cm i.d. was located at a height of 2.4 m. An influent water pipe could be connected to any of these entrances to maintain a constant drop height. The other entries were sealed when not in use.

Compressed air was supplied to the drop chamber headspace to simulate the natural ventilation which can occur in wastewater collection systems and related hydraulic structures. The air flowrate was regulated using a rotameter upstream of its entry into the drop chamber headspace (at a height of 1.8 m above the chamber floor). Air flowrate was verified using a hot-wire anemometer which was inserted into the drop chamber exhaust vent.

The experimental system consisted of three sampling locations: 1) liquid sample valve immediately upstream of water entry into the drop chamber, 2) liquid sample riser pipe located immediately downstream of water discharge from the drop chamber, and 3) gas sample port on exhaust vent. The latter was used for insertion of adsorbent tubes to collect headspace gas samples.

## Experimental Procedure

Each experiment was completed using a tracer cocktail containing four VOCs: ethylene dibromide (EDB), deuterated chloroform (CDCl<sub>3</sub>), toluene and 1,1,1-trichloroethane (TCA). The tracer cocktail was prepared and stored in a Tedlar reservoir 24 hours in advance of each experiment. During preparation, the bag was first evacuated of all air prior to being filled with at least 23 l of distilled water using a peristaltic pump and Teflon transport tubing. During the filling procedure, precise quantities of each volatile tracer were injected using a gas-tight syringe punctured into the transport tubing immediately upstream of its connection with the



Tedlar bag entry valve. To ensure the integrity of tracers stored in the Tedlar reservoir, liquid samples were collected from the reservoir immediately prior to and after each pilot experiment.

During the start of each experiment, desired water flowrate, tailwater depth, and headspace ventilation rates were established and recorded. Following the collection of background samples, tracer injection was initiated at a pre-set injection rate (usually 40 ml/min), and initial injection time was recorded. The system was then allowed to reach a steady-state condition during a time period corresponding to a minimum of 3.5 hydraulic/aerodynamic residence times of the tailwater pool and chamber headspace.

At steady-state, at least three sequential liquid samples were collected upstream and downstream of the drop chamber. All liquid samples were collected with zero headspace in thermally-conditioned 40 ml amber vials with Teflon-lined screw caps. At least two steady-state gas samples were also collected from the exhaust vent sample port during each experiment. Gas samples were collected using Carbotrap 300 multi-bed adsorbent tubes (6 mm i.d., stainless steel walls) and SKC model 224-PCXR7 programmable air sampling pumps. A bubble flowmeter was used downstream of the adsorbent tube to quantify air flowrates and associated sample volumes drawn through each adsorbent tube. In general, sample flowrates varied from 30 ml/min to 120 ml/min, with sample volumes varying from 100 to 1000 ml depending on headspace ventilation and anticipated gaseous VOC concentrations. Following sample collection, adsorbent tubes were capped at each end using stainless-steel plugs. Each tube was then placed in a hermetically sealed glass container and stored in an ice chest for transport to the University of Guelph. Once at the lab, adsorbent tubes were refrigerated at 4 °C until analysis.

### Sample Analysis

All samples were analyzed in the Trace Contaminants Analysis Laboratory at the University of Guelph. Modified USEPA methods 624 and TO-1 were used for liquid and gas samples, respectively. A Tekmar LSC 2000 purge and trap (PAT)/thermal desorption system interfaced with a Hewlett Packard 5890 Series II Gas Chromatograph (GC) and a Hewlett Packard 5971 Mass Selective Detector (mass spectrometer) (MS) were used to analyze all samples. A DB-5 30 m capillary column (0.20 mm i.d. and 1.0 µm film thickness) was used for all analyses. Liquid samples were purged directly from the PAT sparging vessel. Gas samples were analyzed by inserting adsorbent tubes in place of the normal internal concentrating trap within the PAT, with subsequent thermal desorption and sweep to the GC.

The PAT sequence used for each sample was: 7.00 minute dry purge with ultra-high purity (UHP) charcoal polished helium at 100 ml/min, 2.50 minute sample preheat to 200 °C, and 3.25 minute sample desorb. The internal concentrating trap was then swept at 100 ml/min for 2.50 minutes with UHP charcoal-polished helium, and the moisture control module was cooled to 6 °C. The trap was preheated to 195 °C and desorbed for 2.50 minutes at 200 °C. The GC was set to room temperature during this period. All line and valve temperatures were held constant at 150 °C.

The GC sequence was: 31 °C for 2.50 minutes, 40 °C/min to 40 °C for 1.00 minutes, 9.0 °C/min to 120 °C, and 40 °C/min to 200 °C for 2.00 minutes. All analyses were completed in selected ion monitoring (SIM) mode, and the MS was tuned optimally for bromofluorobenzene. Three- to five-point external calibration curves were developed for each set of liquid and gas samples. Whenever a sample exceeded the dynamic range of a standard curve, a smaller volume of duplicate sample was analyzed. Calibration curves were characterized by  $R^2$  ranging from 0.95 to 0.999.

### System Operating Conditions

Volatile tracer experiments were completed using seven system operating conditions as listed in Table I. Over all experiments, liquid flowrate varied from 8.1 to 16.2 m<sup>3</sup>/hr, headspace ventilation rate varied from 14 to 41 m<sup>3</sup>/hr, drop height varied from 1.1 to 1.6 m, tailwater depth was held constant at 0.5 m, and water temperature varied from 10.5 to 17.5 °C.

For the temperatures listed in Table I, values of  $H_c$  were calculated based on Ashworth *et al.*<sup>13</sup> as listed in Table II. For all experiments, upstream liquid concentrations of each tracer were maintained at a constant value greater than 40 mg/m<sup>3</sup>. Gaseous concentrations in the chamber headspace varied from a minimum of 0.02 mg/m<sup>3</sup> (EDB) to a maximum of 4.7 mg/m<sup>3</sup> (TCA). Hydraulic residence time varied from a low of 3.5 minutes (experiments 2-4) to a high of 7 minutes (experiments 5-7).

### RESULTS AND DISCUSSION

Stripping efficiency ( $1 - C_2/C_1$ ), system mass transfer coefficient ( $K_La$ ), ratio of gas-to-liquid phase mass transfer coefficients ( $k_g/k_l$ ), and the product of air entrainment rate and bubble saturation ( $Q_e\gamma$ ) were calculated for each compound and experimental condition.

#### Stripping Efficiencies

For each contaminant and experiment, percentage stripped (stripping efficiency) was calculated based on Equation 7. Resulting values are presented in Table III. As expected, stripping efficiency generally increased with increases in Henry's law coefficient ( $H_c$ ), ventilation rate, and drop height. The only exceptions were slightly higher stripping efficiencies for the slightly lower ventilation rate in experiment 6 as compared with experiment 7, and higher stripping efficiencies for CDCl<sub>3</sub> relative to toluene in experiments 5 and 6.

From these results it is quite clear that lower volatility contaminants (in terms of relative  $H_c$ ) such as EDB can have significantly lower stripping efficiencies than higher volatility VOCs at drop structures. Furthermore, higher volatility VOCs such as 1,1,1-trichloroethane may have stripping efficiencies that far exceed those predicted for relatively long stretches of gravity-flow sewer reaches.<sup>7</sup> Thus, it is likely that individual drop structures serve as major contributors to gas-liquid mass transfer in sewers. Therefore, general efforts to minimize VOC emissions from sewers should focus on such structures.

#### System Mass Transfer Coefficients

For each experiment, system mass transfer coefficients ( $K_La$ ) were calculated based on Equation 11. The lowest mass transfer coefficients were observed for EDB, with values ranging from 0.01/hr (experiment 1) to 0.19/hr (experiment 6). The highest mass transfer coefficients were observed for TCA, with values ranging from 0.42/hr (experiment 1) to 3.7/hr (experiment 6). The experimental sensitivity of  $K_La$  and stripping efficiency to  $H_c$  suggests that air entrainment had a significant influence on gas-liquid mass transfer and/or gas-phase resistance to mass transfer was very important at lower  $H_c$ .

To illustrate the relative significance of gas and liquid-phase mass transfer coefficients, Equations 12 and 13 were applied to experiments 2-4. For this analysis, it was assumed that gas phase resistance to mass transfer was negligible relative to liquid-phase resistance for the most volatile tracer TCA. Thus, it was assumed that for TCA,  $K_La$  was approximately equal to  $k_la$ . Equation 13 was then used to estimate  $k_la$  for each of the other three volatile tracers, allowing use of the inverse of Equation 12 to estimate  $k_g/k_l$ . This approach yields an upper-bound on

$k_g/k_l$ , since  $K_La$  (TCA) is always less than the actual  $k_l a$  (TCA) due to the presence of some gas-phase mass transfer resistance.

Results of the  $k_g/k_l$  analysis are provided in Figure 3. With the exception of  $CDCl_3$  and toluene at the lowest ventilation rate, the ratio of  $k_g/k_l$  increased with an increase in  $H_c$ . For all three tracers, the ratio increased with increasing ventilation rate. Finally, the conservative values of  $k_g/k_l$  obtained in this study (ranging from 0.6 to 15 over all compounds and experiments) were much lower than values of 40 to 300 typically reported for natural and engineered water and wastewater systems.<sup>15-17</sup> This is an important finding since it is commonly assumed that gas-phase resistance to mass transfer is small (less than 10%) relative to liquid-phase resistance for  $H_c$  greater than 0.1. For  $k_g/k_l$  of 10, Equation 2 indicates that gas phase resistance to mass transfer would account for 85%, 53%, 34%, and 18% of overall resistance to mass transfer for EDB ( $H_c = 0.017$ ),  $CDCl_3$  ( $H_c = 0.089$ ), toluene ( $H_c = 0.19$ ) and TCA ( $H_c = 0.46$ ), respectively, at 13 °C.

### Effects of Headspace Ventilation

Equations 7 and 8 indicate that the product of ventilation rate ( $Q_g$ ) and Henry's law coefficient ( $H_c$ ) is an important parameter for predicting stripping efficiencies in enclosed drop structures. Values of percent stripped versus  $Q_g H_c$  are plotted in Figure 4 for experiments 2-4 and experiments 5-7. For both sets of experiments, there is a clear trend of increased stripping with increased  $Q_g H_c$ , consistent with an increase in the  $f$  factor of Equations 7 and 8. With the exception of one data point, stripping efficiency values for experiments 2-4 appeared to "level off" at higher values of  $Q_g H_c$ , which is consistent with an approach to infinite ventilation conditions, e.g. a drop structure open to the atmosphere. A similar trend was not evident for experiments 5-7.

The results presented in Figure 4 illustrate the importance of properly quantifying both chemical volatility, as measured by  $H_c$ , and headspace ventilation rate for predicting VOC emissions at drop structures. For compounds of low volatility and/or poor sewer ventilation conditions, an assumption of infinite ventilation may lead to order-of-magnitude overestimates of VOC emissions.

### Effects of Liquid Flowrate

To assess the impact of liquid flowrate, results from experiments 4 and 7 were compared. Experiment 4 had a liquid flowrate twice that of experiment 7. Because of a slightly higher ventilation rate (41 versus 38 m<sup>3</sup>/hr) and temperature (17.5 versus 13 °C) for experiment 7, values of  $Q_g H_c$  were slightly higher for all compounds in experiment 7. However, differences in  $Q_g H_c$  between the two experiments ranged from between 21 and 29%. According to Figures 4, such differences should not affect stripping efficiency significantly for  $Q_g H_c$  greater than approximately 3. This criteria was true for all tracers other than EDB.

A bar chart depicting  $K_La$  versus tracer compound for experiments 4 and 7 is provided in Figure 5. For all tracers, overall system mass transfer coefficients were greater under conditions of higher water flowrate. Despite the effects of liquid flow on  $K_La$ , stripping efficiency was greater under low flow conditions than under high flow conditions, as shown in Figure 6. This is not consistent with the experimental results presented by Pincince<sup>5</sup> for primary and secondary clarifier weirs, and by Nakasone<sup>12</sup> for drops under low flow conditions. However, their models do not account for hydraulic residence time in a tailwater pool. The hydraulic residence time was approximately a factor of two higher for experiment 7 relative to experiment 4. This characteristic is accounted for by Equation 7, which includes the product of both  $K_La$  and hydraulic residence time.

### Effects of Drop Height

The liquid flowrate for experiment 1 (11 m<sup>3</sup>/hr) was lower than the flowrate (16 m<sup>3</sup>/hr) used in experiments 2-4. Thus, all other factors being equal, the results depicted in Figure 6 suggest that stripping efficiency should have been greater for experiment 1. However, experiment 1 was characterized as having a 31% lower drop height (1.1 m) compared with all other experiments (1.6 m). This difference had a significant influence on VOC stripping efficiency as indicated in Figure 7. For similar values of  $Q_e H_c$ , stripping efficiencies for experiment 1 were a factor of 3 to 4 lower than stripping efficiencies observed for experiments 2-4. Similarly, system mass transfer coefficients ( $K_L a$ ) were a factor of 4 to 8 lower for experiment 1.

### Air Entrainment as a Mass Transfer Mechanism

Nakasone<sup>12</sup> estimated that greater than 90% of oxygen transfer at a weir is due to air entrainment caused by falling water that impacts an underlying tailwater. McLachlan *et al.*<sup>18</sup> assumed that air entrainment at large waterfalls accounts for all emissions from such systems. Furthermore, they assumed that for all VOCs  $\gamma = 1$  (bubbles fully saturated) and  $Q_e/Q$  varies from 5 to 30. These assumptions were used to estimate VOC emissions from Niagara Falls. Finally, Mihelcic *et al.*<sup>4</sup> provided an example calculation of VOC emissions from a clarifier weir and assumed a  $Q_e/Q$  value of 0.03. No verification or argument to support this value was provided.

For the pilot experiments described in this paper it was not possible to separate the values of  $Q_e$  and  $\gamma$ . However, conservative (upper-bound) estimates of  $Q_e/Q$  were determined using Equation 21, normalized by  $Q$ , and the following assumptions:

1. All emissions were caused by air entrainment.
2. Rising air bubbles were saturated ( $\gamma = 1.0$ ) with respect to each tracer.

Results are shown in Table IV. The value of  $\gamma$  should have increased with decreasing  $H_c$ . Thus, assumption 2 above should have been most valid for EDB. However, gaseous concentrations of EDB were generally close to method detection limits and were therefore characterized by higher variations and more uncertainty than the other three tracers. This trend is evident in the ranges reported in Table IV. With the exception of toluene and TCA during experiments 5-7,  $Q_e/Q$  generally decreased with increasing  $H_c$  as expected.

Use of CDCl<sub>3</sub> to estimate  $Q_e/Q$  resulted in values similar to those obtained using EDB, and generally greater than values obtained using toluene and TCA. For experiment 1,  $Q_e/Q$  and  $Q_e$  estimates were all lower than for experiments 2-7, which is consistent with a lower drop height. In general,  $Q_e$  was approximately 1 and  $Q_e/Q$  was approximately 0.1 for experiment 1, with slight variations between tracers. Values of  $Q_e$  were similar for experiments 2-4 and 5-7, ranging from 5-8 m<sup>3</sup>/hr and 4-14 m<sup>3</sup>/hr, respectively for CDCl<sub>3</sub>. Because of higher liquid flowrates for experiments 2-4, values of  $Q_e/Q$  were lower (0.3-0.5) compared with experiments 5-7 (0.5-1.7) for CDCl<sub>3</sub>.

In general, values of  $Q_e/Q$  ranged over approximately one order of magnitude for the seven pilot experiments. The values were intermediate between the extremes of a small clarifier weir and a very large waterfall.<sup>4,18</sup>

## SUMMARY AND CONCLUSIONS

Pilot experiments were completed using four volatile compounds to study gas-liquid mass transfer at enclosed sewer drop structures. Stripping efficiencies and system mass transfer coefficients for the four VOCs and several operating conditions were presented. Effects of contaminant physicochemical properties were described in terms of Henry's law coefficients. For all experiments, stripping efficiency was directly proportional to the product of headspace ventilation and Henry's law coefficient, with maximum stripping efficiency as high as 46% for 1,1,1-trichloroethane.

The major conclusions which follow from this research are:

1. Stripping efficiencies and mass transfer coefficients for VOCs at sewer drop structures are a strong function of compound physicochemical properties, particularly Henry's law coefficient. This suggests the potential importance of air entrainment as a mass transfer mechanism.
2. Ratios of gas to liquid phase mass transfer coefficients for some sewer drop structures are much lower than those reported for other water and wastewater treatment processes.
3. Stripping efficiencies are significantly affected by the finite ventilation conditions associated with many sewer atmospheres, and attempts to model emissions from sewer drop structures using open (infinite) ventilation conditions can lead to significant overestimates of such emissions.
4. Stripping efficiencies are significantly affected by hydraulic residence time in tailwater pools at the bottom of drop structures. This may be true even when the magnitude of system mass transfer coefficients and/or air entrainment rates are reduced for low water flowrates.
5. Existing models to estimate oxygen transfer at weirs and other drop structures are not appropriate for use in estimating VOC emissions from drop structures characterized by an accumulation of tailwater, e.g. pump station wet wells.
6. Based on the experimental results presented in this paper and predictions from previous modeling studies, drop structures are likely to be the dominant source of gas-liquid mass transfer in municipal and industrial sewers.

Additional studies involving mass transfer of oxygen and a cocktail of 10 volatile and semi-volatile organic compounds are now underway. Primary objectives are to assess the potential for relating easily obtainable oxygen transfer information to VOC transfer at drop structures, and to ascertain the relative significance of air entrainment as a transfer mechanism under various drop structure operating conditions. These experiments are being completed both at the pilot scale and in operating municipal sewers in Southern Ontario.

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**Table I.** System operating conditions for pilot experiments.

Expt	Drop Height (m)	Tailwater Depth (m)	Flowrates (m <sup>3</sup> /hr)	
			Liquid	Gas
1	1.1	0.5	11	31
2	1.6	0.5	16	14
3	1.6	0.5	16	26
4	1.6	0.5	16	38
5	1.6	0.5	8.1	19
6	1.6	0.5	8.1	32
7	1.6	0.5	8.1	41

**Table II.** Henry's law coefficients as estimated by Ashworth *et al.*<sup>13</sup>.

Expt	Water T (°C)	Henry's Law Coefficient, H <sub>c</sub>			
		EDB	CDCI3	Toluene	TCA
1	10.5	0.015	0.077	0.17	0.42
2-4	13.0	0.017	0.089	0.19	0.46
5-7	17.5	0.020	0.12	0.22	0.54

**Table III.** Stripping efficiencies during each pilot experiment.

Expt	Stripping Efficiency (%)			
	EDB	CDCI3	Toluene	TCA
1	0.1	1.0	1.6	2.6
2	0.3	3.4	3.8	12
3	0.4	2.9	4.7	10
4	0.9	4.2	6.6	9.0
5	0.4	11	6.8	31
6	3.1	21	11	44
7	2.3	9.5	9.7	29



Table IV. Estimates of air entrainment rate ( $Q_e$ ) normalized by liquid flowrate ( $Q$ ).

Compound/Expt --->	1	$Q_e/Q$	
		2-4	5-7
EDB	0.06	0.10-0.57	0.15-1.0
$\text{CDCl}_3$	0.14	0.33-0.51	0.49-1.7
Toluene	0.11	0.22-0.42	0.23-0.37
TCA	0.08	0.23-0.39	0.36-0.79

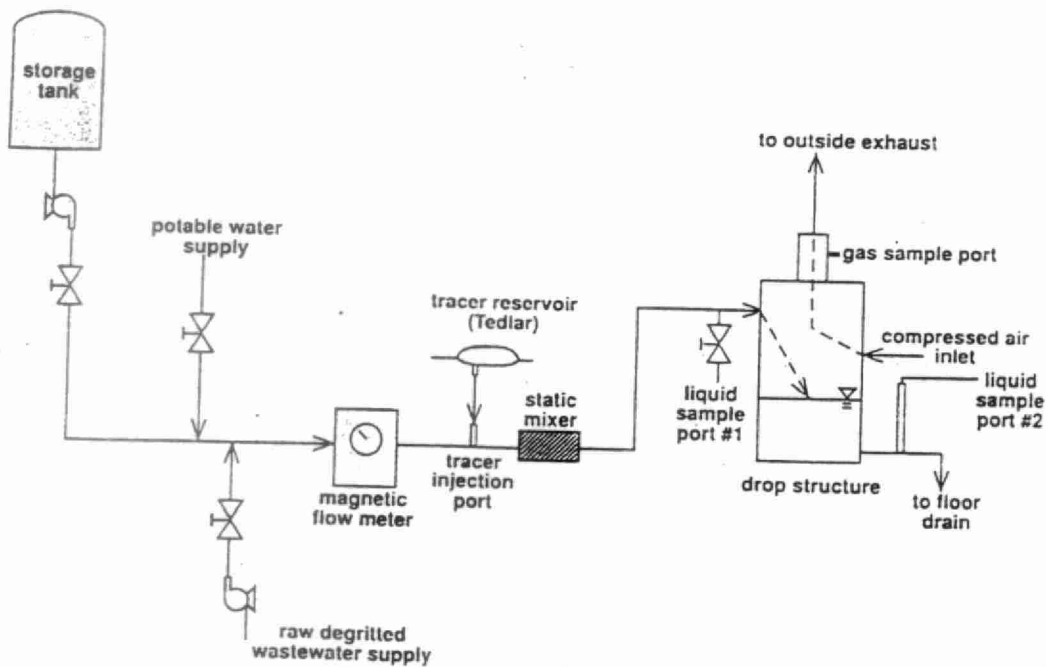


Figure 1. Flow diagram of experimental system.

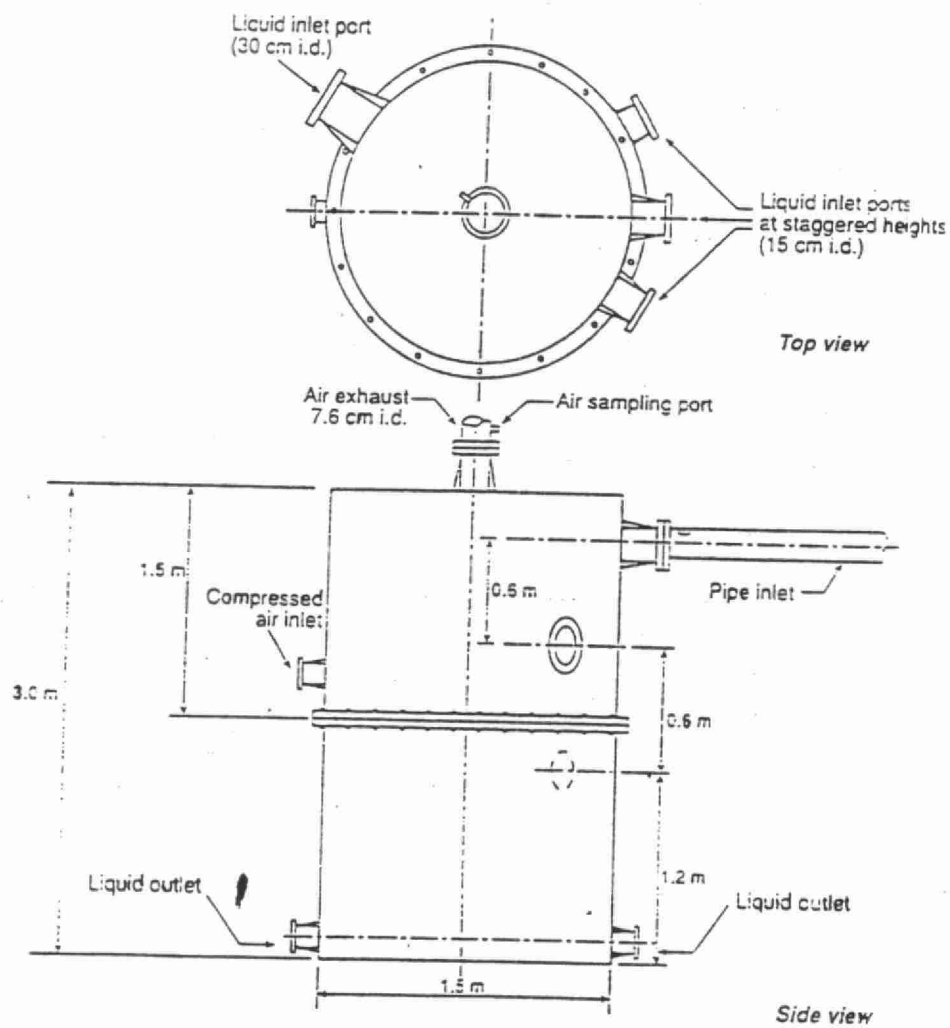


Figure 2. Major components and dimensions of pilot drop chamber.

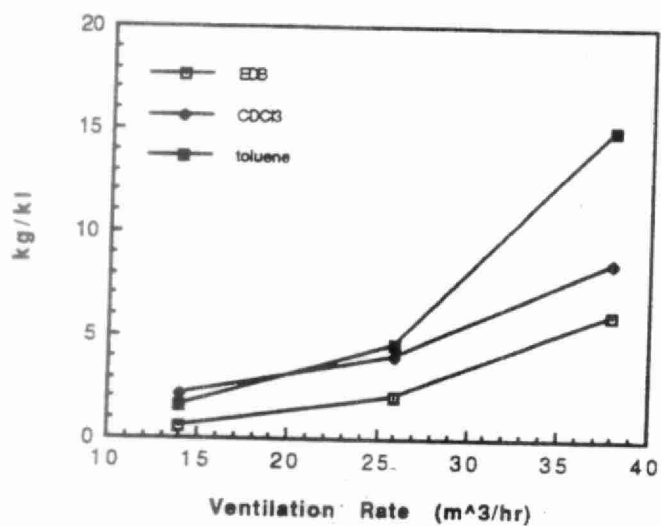


Figure 3. Ratio of gas- to liquid-phase mass transfer coefficients versus ventilation rate (experiments 2-4).

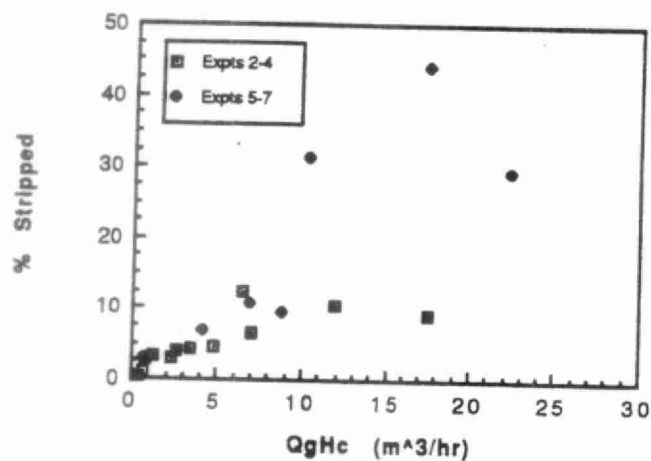
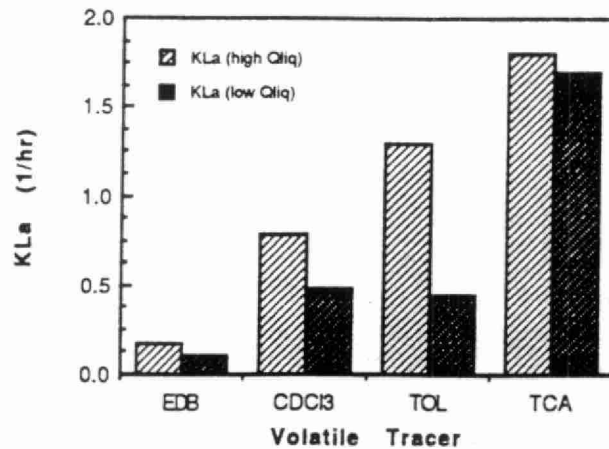
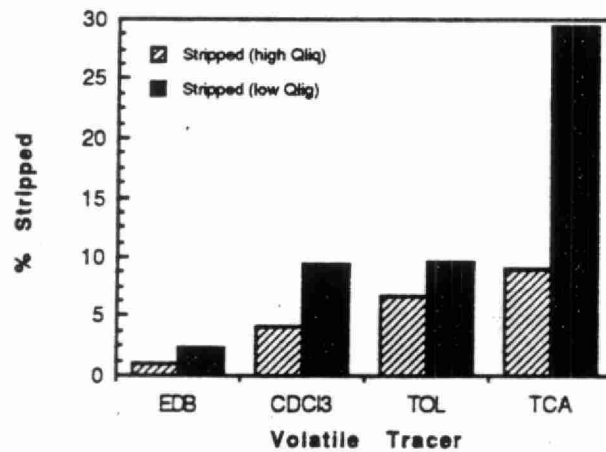


Figure 4. Stripping efficiency versus the product of headspace ventilation rate and Henry's law coefficient (experiments 2-4 and 5-7).



**Figure 5.** System mass transfer coefficients for low water flow (experiment 7) and high water flow (experiment 4) conditions.



**Figure 6.** Stripping efficiencies for low water flow (experiment 7) and high water flow (experiment 4) conditions.

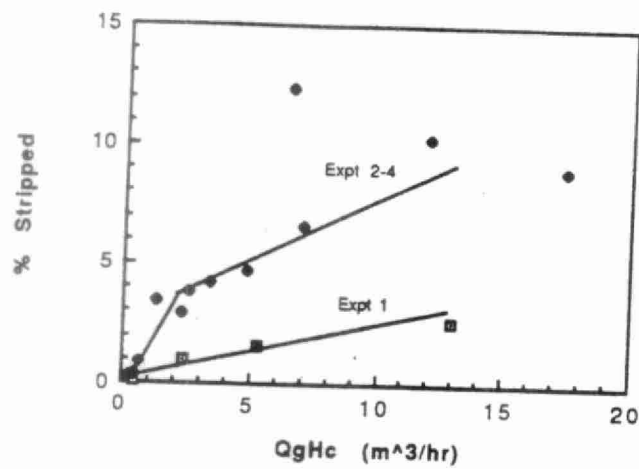


Figure 7. Stripping efficiency versus the product of headspace ventilation rate and Henry's law coefficient (experiments 1 and 2-4).

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## **Volatile and Semi-Volatile Organic Compound Emissions from Sewer Drop Structures**

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## INTRODUCTION

Volatile organic compounds (VOCs) and semi-VOCs are discharged to municipal wastewater from a large number of sources, including various commercial and industrial facilities, residential households, and public institutions. Concerns regarding the occurrence of VOCs and semi-VOCs in wastewater include potentially adverse effects on downstream biological treatment and ultimate environmental receiving systems. However, recent studies have raised new concerns regarding airborne emissions of VOCs and semi-VOCs, including:<sup>1</sup>

1. Many VOCs and semi-VOCs are considered to be toxic air contaminants (TACs) that can pose inhalation exposure risks to treatment plant employees and, in the case of significant localized emissions, to the general public.
2. Many VOCs and semi-VOCs are considered to be highly reactive organic gases (ROGs) that can contribute to the production of ozone in photochemically active urban atmospheres.
3. With sufficient gaseous accumulation in sewers, many VOCs and semi-VOCs pose explosion hazards.

The validity of the latter concern has been well-documented through extreme and sometimes tragic historical events. However, the significance of municipal wastewater as a source of TAC and ROG emissions to the ambient atmosphere has not been determined. Furthermore, past studies have focussed on VOC emissions from wastewater treatment systems, and there is a paucity of existing literature related to emissions from wastewater collection systems (WCS).<sup>2-4</sup>

This paper provides a summary of ongoing research to improve existing knowledge related to stripping of VOCs and semi-VOCs from wastewater to overlying sewer atmospheres. The focus of this paper is on gas-liquid mass transfer at sewer drop structures. Mass transfer along uniform sewer reaches is presented in a companion paper.<sup>5</sup>

## BACKGROUND

Gas-liquid mass transfer of VOCs and semi-VOCs can be classified as occurring at two general locations in WCS: 1) along relatively-uniform flowing sewer reaches, e.g. interceptor channels, and 2) at points of rapid dissipation of potential energy, e.g. drop manholes or free-fall drops into pump station wet wells. In either case, the rate of gas-liquid mass transfer between wastewater and a sewer atmosphere can be represented mathematically as

$$m_T = K (C_l - \frac{C_g}{H_c}) A, \quad (1)$$

where

- $m_T$  = mass transfer rate across wastewater-air interface (mg/s)
- $K$  = overall mass transfer coefficient (m/s)
- $C_l$  = concentration of contaminant in the liquid phase (mg/m<sup>3</sup>)
- $C_g$  = concentration of contaminant in the gas phase (mg/m<sup>3</sup>)
- $H_c$  = compound-specific dimensionless Henry's law constant (-)
- $A$  = area of wastewater-air interface (m<sup>2</sup>).

The inverse of overall mass transfer coefficient can be written in terms of liquid and gas phase mass transfer resistances such that

$$\frac{1}{K} = \frac{1}{k_l} + \frac{1}{k_g H_c} \quad (2)$$

where

- $k_l$  = liquid-phase mass transfer coefficient (m/s)
- $k_g$  = gas-phase mass transfer coefficient (m/s).

Equations 1 and 2 account for two important phenomena. First, in confined sewers the mass transfer rate can be significantly affected by contaminant accumulation in the gas phase. Thus, the effects of sewer ventilation on  $C_g$  are potentially very important. Second, if  $k_g H_c$  is much greater than  $k_l$ , it is reasonable to approximate  $K = k_l$ . This is generally assumed to be valid for  $H_c$  greater than 0.1. However, for  $H_c$  less than 0.1,  $K H_c$  is generally not significantly greater than  $k_l$ , and gas-phase resistance to overall mass transfer becomes important. This  $H_c$  criteria is hereafter used to distinguish between VOCs ( $H_c > 0.1$ ) and semi-VOCs ( $H_c < 0.1$ ).

## Mechanisms of Mass Transfer at Sewer Drop Structures

Several mechanisms can contribute to gas-liquid mass transfer at sewer drop structures, and are illustrated in Figure 1. Mass transfer can occur at

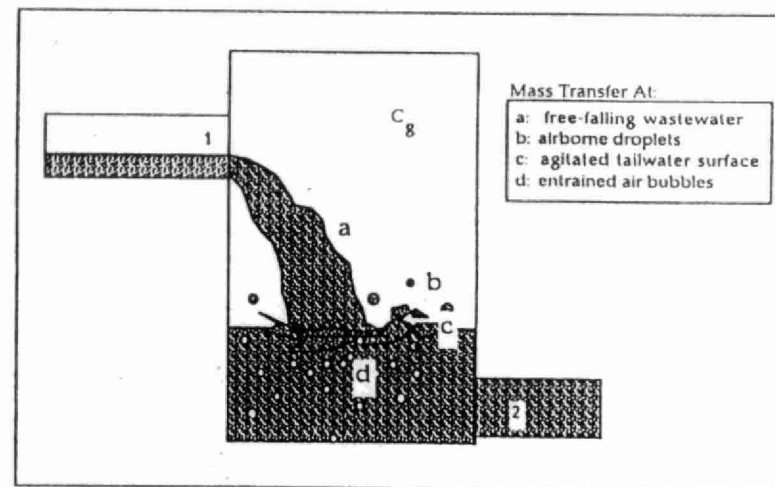


FIGURE 1. Mechanisms of gas-liquid mass transfer at sewer drop structures.

- the free-falling wastewater surface,
- splashing and airborne droplets generated at the surface of the receiving tailwater,
- agitated tailwater surface, and
- air bubbles entrained in the tailwater.

Problems associated with application of Equations 1 and 2 to drop structures are 1) there is effectively no available published literature which describes mass transfer coefficients for each of the four primary transfer mechanisms listed above, 2) it is difficult to ascertain the effective surface area associated with each of the transfer mechanisms, and 3) there is a paucity of existing literature associated with natural ventilation of WCS, i.e. as it affects  $C_g$ . Thus, existing models of mass transfer at drop structures are highly empirical, and general extrapolation of these models is characterized by a high degree of uncertainty. Furthermore, such models have focussed on oxygen transfer to clean water flowing through open systems.<sup>6-8</sup> They have not been rigorously evaluated for applications involving VOCs or semi-VOCs in enclosed wastewater collection systems.

#### Empirical Deficit Models (EDM)

The most common models for predicting oxygen transfer at drop structures involve empirical expressions of the form:<sup>8-9</sup>

$$r_o = \frac{C_{so1} - C_{o1}}{C_{so2} - C_{o2}} = F\left(\frac{Q}{w}, h, z\right), \quad (3)$$

where

- $r_o$  = oxygen deficit ratio (-)
- $C_{so1}$  = saturation oxygen concentration upstream of drop (mg/l)
- $C_{so2}$  = saturation oxygen concentration downstream of drop (mg/l)
- $C_{o1}$  = actual dissolved oxygen concentration upstream of drop (mg/l)
- $C_{o2}$  = actual dissolved oxygen concentration downstream of drop (mg/l)
- $F$  = denotes functional operator
- $Q$  = water flow rate over drop ( $m^3/hr$ )
- $w$  = width of weir or drop at point of initial water fall (m)
- $h$  = drop height (m)
- $z$  = tailwater depth (m).

If it is assumed that mass transfer to entrained air bubbles is small relative to other mass transfer mechanisms shown in Figure 1,  $r_o$  can be related to an analogous term for VOCs according to

$$r_v = r_o \alpha \Psi, \quad (4)$$

$$r_v = \frac{C_1 - \frac{C_g}{H_c}}{C_2 - \frac{C_g}{H_c}}, \quad (5)$$

$$\Psi = \left\{ \frac{D_v}{D_o} \right\}^n, \quad (6)$$

where

- $r_v$  = VOC deficit ratio (-)
- $\alpha$  = transfer coefficient ratio between wastewater and clean water (-)
- $C_1$  = Aqueous VOC concentration upstream of drop ( $mg/m^3$ )
- $C_2$  = Aqueous VOC concentration downstream of drop ( $mg/m^3$ )
- $C_g$  = Gaseous VOC concentration above drop ( $mg/m^3$ )
- $D_v$  = liquid-phase diffusion coefficient of VOC ( $m^2/s$ )
- $D_o$  = liquid-phase diffusion coefficient of oxygen ( $m^2/s$ )
- $n$  = exponent ranging from 0.5 to 1.0 (i.e., two-film to penetration theories).

Furthermore, Corsi and Card<sup>10</sup> used Equation 5 with a simultaneous mass balance on a well-mixed head space to derive the following relationship for VOC concentration downstream of a drop structure:

$$C_2 = \frac{\frac{C_1}{r_v} - \frac{C_1 Q}{H_c Q_v} \left[ \frac{1}{r_v} - 1 \right]}{1 - \frac{Q}{H_c Q_v} \left[ \frac{1}{r_v} - 1 \right]}, \quad (7)$$

where

- $Q_v$  = headspace ventilation rate ( $m^3/hr$ ).

It is significant that Equations 4 through 7 are only valid for VOCs, as their derivation from oxygen transfer models does not account for gas-phase resistance to mass transfer, i.e. oxygen is a highly volatile compound. It is conceivable that Equation 4 can be adjusted to account for gas-phase resistance such that

$$r_v = r_o f \alpha \Psi, \quad (8)$$

where

$$f = \frac{1}{1 + \frac{k_l}{k_g H_c}} \quad (9)$$



from two-film theory. However, Equation 9 would only be valid if the ratio  $k_g/k_l$  was equal for each mass transfer process in Figure 1. Values of  $k_g/k_l$  have been observed to be between 100 and 150 for VOCs in many gas-liquid contacting systems.<sup>11</sup> Values of  $k_g/k_l$  as low as 40 have been reported for VOCs in mechanical surface aeration systems.<sup>12</sup> Such systems are characterized by high specific power input that might be representative of potential energy dissipation in large drop structures. However, values of  $k_g/k_l$  have not been cited for drop structures and raw wastewater. Furthermore, even for VOCs, Equations 4 through 7 must be used with caution if mass transfer to entrained air bubbles is significant. This is because oxygen transfer is not likely to approach equilibrium conditions between air bubbles and surrounding wastewater, which is possible for VOCs. This mass transfer effect has not been acknowledged in the existing literature.

#### Mechanistic Component Models (MCM)

A novel approach to estimation of gas-liquid mass transfer at drop structures would be to separate each mass transfer process into contributing terms in a general mass balance. Thus, for steady-state conditions

$$E = wK_a \int_1^2 \left( C_v - \frac{C_g}{H_c} \right) dh + (K_b + K_c) \left( C_2 - \frac{C_g}{H_c} \right) A + Q_e \gamma C_2 H_c - QC_g \quad (10)$$

where

- $E$  = contaminant emission rate (mg/hr)
- $K_a$ ,  $K_b$ , and  $K_c$  = overall mass transfer coefficients for processes a, b, and c, respectively (m/hr)
- $C_v$  = contaminant concentration as a function of distance along the falling waterfall (mg/m<sup>3</sup>)
- $h$  = fall height (m)
- $A$  = combined effective surface area of tailwater and airborne droplets (m<sup>2</sup>)
- $Q_e$  = air bubble entrainment rate (m<sup>3</sup>/hr)
- $\gamma$  = degree of saturation of air bubbles (-),

and all other variables are as defined previously.

The first term on the right hand side of Equation 10 represents mass transfer between the falling wastewater and adjacent sewer air. Since the aqueous contaminant concentration varies from the top to the bottom of the drop, the transfer process must be integrated from top to bottom (1 to 2). Here, it is assumed that  $w$  and  $K_a$  are independent of fall height. This is also true for  $C_g$  and  $H_c$ , which have been retained inside the integral for brevity. The second term on the right hand side combines the effects of mass transfer to/from airborne droplets and to/from the tailwater surface. The third term represents mass transfer to entrained air bubbles, which may ( $\gamma = 1$ ) or may not ( $\gamma < 1$ ) be in equilibrium with the surrounding wastewater. The final term represents pre-contamination of air, i.e. headspace air, entrained into the tailwater.

It is important to recognize that steady-state MCM emissions estimates would require use of Equation 10 along with a simultaneous mass balance on the gas phase. Unfortunately, there is a general lack of information regarding five factors in Equation 10:  $K_a$ ,  $K_b$ ,  $K_c$ ,  $Q_e$ , and  $\gamma$ . Therefore, it would be valuable to identify specific conditions in which some terms in Equation 10 can be assumed to be negligible, or conversely dominant, thus simplifying future applications and research aimed at MCM development.

#### Lumped System Models (LSM)

Here, we define a lumped system model for mass transfer at drop structures as one based on Equation 2, with the assumption that the overall mass transfer coefficients for transfer mechanisms shown in Figure 1 can be "lumped" into a single "system" mass transfer coefficient  $K_s$ . For this study, it is assumed that contaminant losses from the liquid phase are small, so that the application of an upstream/downstream average concentration ( $C_{av}$ ) for  $C$  in Equation 2 introduces no more than a 10-20% error in back-calculation of  $K_s$ . Then, steady-state mass balances on the gas and liquid phases of an enclosed drop structure yield

$$\text{Liquid: } QC_1 - QC_2 - K_s \left( C_{av} - \frac{C_g}{H_c} \right) = 0, \quad (11)$$

and

$$\text{Gas: } Q_v C_{g,i} - Q_v C_g + K_s \left( C_{av} - \frac{C_g}{H_c} \right) = 0, \quad (12)$$

where

- $C_{g,i}$  = gaseous contaminant concentration conveyed into headspace from ambient air (mg/m<sup>3</sup>)
- $K_s$  = overall system mass transfer coefficient (m<sup>3</sup>/hr)
- $C_{av}$  = average of upstream and downstream contaminant concentrations =  $\frac{C_1 + C_2}{2}$  (mg/m<sup>3</sup>).

The interfacial area of the entire system has been "lumped" into  $K_s$ .

Finally, if it is assumed that  $C_{g,i} \ll C_g$ , Equations 11 and 12 can be solved simultaneously for steady-state emissions such that

$$E = QC_1 \left\{ 1 - \frac{Q - \frac{K_s}{2} \left[ 1 + \frac{1}{H_c} \left\{ \frac{1}{\frac{Q_v}{K_s} + \frac{1}{H_c}} \right\} \right]}{Q + \frac{K_s}{2} \left[ 1 + \frac{1}{H_c} \left\{ \frac{1}{\frac{Q_v}{K_s} + \frac{1}{H_c}} \right\} \right]} \right\} \quad (13)$$

Furthermore, solution of Equation 11 for  $K_s$  yields

$$K_s = \frac{Q(C_1 - C_2)}{C_{av} - \frac{C_g}{H_c}} \quad (14)$$

Thus, measurements of upstream, downstream, and gaseous contaminant concentrations can be coupled with measurements of wastewater flow rate to back-calculate  $K_s$  for specific drop structures.

The LSM approach is more intuitive than the EDM approach from a mechanistic standpoint. However, it suffers from similar limitations including 1) the need to estimate  $K_s$ , likely using an empirical estimation method unless  $K_s$  is determined experimentally for a specific system, and 2) an inability to properly adjust  $K_s$  between VOCs and semi-VOCs if transfer to entrained air bubbles is significant.

#### Air Entrainment Models (AEM)

Air entrainment models are based on the assumption that mass transfer at drop structures is dominated by air bubbles entrained in tailwater. Thus, steady-state mass balances on the well-mixed tailwater and headspace of an enclosed drop structure lead to

$$\text{Liquid: } QC_1 - QC_2 - Q_e(\gamma C_2 H_c - C_g) = 0 \quad (15)$$

$$\text{Gas: } Q_v C_{g,i} - Q_v C_g + \gamma Q_e C_2 H_c - C_g Q_e = 0 \quad (16)$$

where all variables are as defined previously. If  $C_{g,i} \ll C_g$ , Equations 15 and 16 can be solved simultaneously to estimate contaminant emissions as

$$E = QC_1 \left\{ 1 - \left[ \frac{1}{1 + \frac{\gamma H_c Q_e}{Q} \left\{ 1 - \frac{Q_e}{Q_e + Q_v} \right\}} \right] \right\}. \quad (17)$$

Equation 17 indicates that emissions are maximum as  $Q_v$  becomes very large, e.g. open systems, thus

$$E = QC_1 \left\{ 1 - \left[ \frac{1}{1 + \frac{\gamma H_c Q_e}{Q}} \right] \right\}. \quad (18)$$

Furthermore, emissions approach influent mass loadings (100% removal) as the ratio  $Q_e/Q$  becomes very large.

Equations 15 and 16 can be used to estimate  $Q_e$  based on measured contaminant concentrations in the liquid and gas phases such that

$$Q_e = \frac{Q(C_1 - C_2)}{\gamma C_2 H_c - C_g} \quad (19)$$

The three major limitations to application of Equation 17 are 1) a lack of knowledge of conditions in which entrainment dominance is a valid assumption, 2) reasonable estimates of  $\gamma$ , or a value of  $H_c$  below which  $\gamma = 1$  is a reasonable assumption, and 3) values of  $Q_e$  for various types of drop structures and liquid flow regimes.

McLachlan *et al.*<sup>13</sup> used Equation 18 with  $\gamma = 1$  to estimate VOC emissions from Niagra Falls. Based on their own and a limited amount of published research, they argued that values of  $Q_e/Q$  should be in the range of 5 to 30 for large waterfalls.

#### PILOT DROP EXPERIMENTS

A series of pilot experiments were completed to study the mechanisms that affect gas-liquid mass transfer at drops. The experimental system, methodologies, and analysis procedures are described below.

##### Experimental Drop Structure

A pilot drop structure (PDS) was constructed and maintained in the Pilot Reactors Laboratory of the Wastewater Technology Centre in Burlington, Ontario. The structure (Figure 2) consists of two fibreglass tanks (1.5 m i.d. x 1.5 m height) connected with a rubber gasket to form an enclosed drop chamber. The system contains three 15 cm i.d. flanged inlet ports separated at 30° angles at heights of 1.2 m, 1.8 m, and 2.5 m above the floor of the system. A fourth 30 cm i.d. inlet port is also located at a height of 2.4 m. Two 7.6 cm i.d. effluent ports are located at the bottom of the tank.

The PDS consists of two liquid influent flow pipes (15 cm and 30 cm i.d. - PVC) that can be connected to the aforementioned flanged inlets. Each inlet pipe is 2 m in length and contains a tracer injection port and tracer/dissolved oxygen sampling port. The former is located 1.5 m upstream of the drop into the enclosed PDS chamber. It consists of a 6 mm i.d. stainless steel tube that extends into the liquid phase (near invert) of the influent pipe, and a Swagelock fitting used to secure tracer injection tubing. The sampling port is located 30 cm upstream of the PDS drop, and consists of a 5 cm diameter hole into which a dissolved oxygen probe can be inserted. Otherwise, the hole is closed using a rubber stopper containing a 6 mm port into which teflon tubing can be threaded to obtain liquid samples.

The PDS can be operated using tap water or raw/degritted wastewater obtained from the City of Burlington's Skyway treatment plant and available at the Wastewater Technology Centre on a flow-through continuous basis. Water and wastewater flows are monitored using a magnetic flow meter, with maximum achievable flow rates of 16 m<sup>3</sup>/hr.

The liquid drain system consists of two 7.6 cm PVC pipes bolted to the bottom drain flanges. One of the two drain pipes consists of a riser that is large enough to insert a dissolved oxygen probe into, and to pump and collect liquid effluent water or wastewater samples.

The headspace of the PDS can be ventilated using compressed air introduced at a ventilation inlet port located 1.3 m above the PDS floor. Inlet ventilation rates are monitored using a rotameter, with maximum achievable air flow rates of 140 m<sup>3</sup>/hr. Ventilation air is exhausted

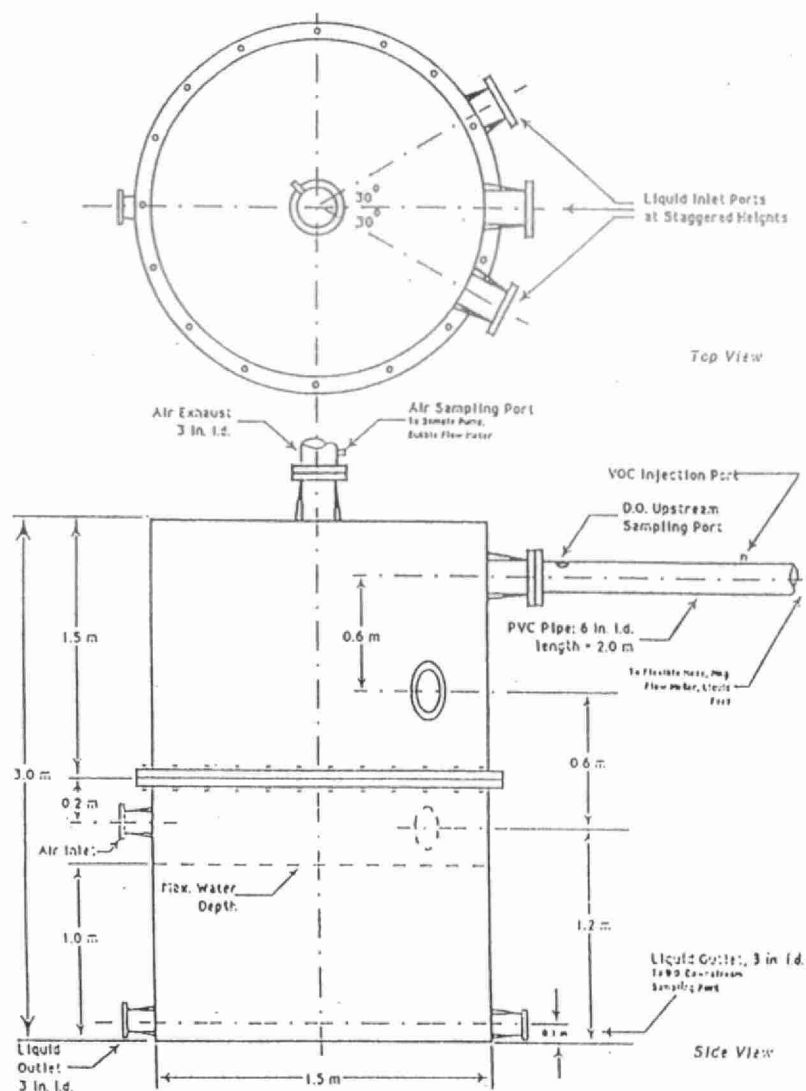


FIGURE 2. Pilot drop structure.

from the PDS headspace using a PVC riser flanged/bolted to the top of the drop structure. An air sampling port consisting of a 6 mm i.d. Swagelock connection is located 30 cm above the base of the ventilation riser, and is used for inserting and securing adsorbent tubes for gas collection.

Prior to completing any experiments, the PDS liquid flow system was analyzed to assess the relationship between liquid flow rate and width at the top of the drop (e.g., for use with functional relationships as described by Equation 3). Thus, experimental values of  $w$  can be obtained through preliminary calibrations and measured values of liquid flow rate ( $Q$ ).

#### Experimental Methodology: Oxygen Experiments

A series of factorial experiments were completed to assess oxygen transfer to wastewater under a range of variations in drop height, tailwater depth, and wastewater flow rate. Dissolved oxygen concentrations were measured upstream and downstream of the drop, and in the PDS headspace using a YSI model 58 digital dissolved oxygen meter. Data were used to assess lumped system mass transfer coefficients ( $K_L$ ) as functions of the aforementioned variables.

#### Experimental Methodology: VOC Experiments

Two preliminary VOC and semi-VOC transfer experiments have been completed to date. Each experiment was completed using a tracer cocktail consisting of deuterated chloroform ( $\text{CDCl}_3$ ) and ethylene dibromide (EDB) injected into wastewater. The dimensionless Henry's law constants of  $\text{CDCl}_3$  and EDB at 25 °C are 0.14 and 0.028, respectively.<sup>14-15</sup> Thus, these two compounds should exhibit a range of relative significance of gas-phase resistance to mass transfer.

The tracer cocktail was prepared by pre-dissolving  $\text{CDCl}_3$  and EDB in tap water, and storing the mixture in a collapsible 5 l tedlar reservoir. This allowed the maintenance of zero headspace prior to and during PDS experiments. The tracer mixture was prepared no more than 48 hours in advance of each experiment, and liquid samples were collected from the bag during experiments to confirm gravimetric tracer concentrations.

During each experiment, the tracer solution was injected into the influent pipe using a peristaltic pump and teflon tubing connected to the aforementioned stainless steel injection system. Tracer injection rates were monitored by measuring the change in volume of the tedlar reservoir over the known experimental time period. This approach provided consistent flow rate results using the same tedlar reservoir and peristaltic pump arrangement in the laboratory.

Liquid samples were collected using a second peristaltic pump with teflon tubing threaded into the pre-drop sample port. Samples were collected in 40 ml glass sample vials with teflon-lined screw caps. Liquid samples were also collected at the bottom of the PDS using the sampling riser described previously and a third peristaltic pump with teflon tubing.

Gas samples were collected in the PDS riser vent using Carbotrap 300 multi-bed adsorbent tubes (6 mm i.d., stainless steel tubes) and SKC model 224-PCXR7 programmable air sample pumps. A bubble flowmeter was used to quantify sample volume over a known time period. Adsorbent tubes were sealed at each end using Swagelock plugs immediately following sample collection. Tubes were then placed in hermetically-sealed glass containers and stored, along with liquid sample vials, in an ice-chest prior to return to the Environmental Engineering Laboratory (EEL) at the University of Guelph.

All liquid and gas samples were refrigerated at 4 °C and allowed to warm to room temperature prior to analysis. Liquid samples were pre-concentrated by purging onto clean adsorbent tubes. All tubes were then analyzed using a Tekmar model LSC 2000 purge and trap plumbed to a Hewlett-Packard model 5890 Series II gas chromatograph with a DB-5 30 m narrow-bore capillary column (0.20 mm i.d. with 1 µm film thickness). A Hewlett-Packard model 5971A mass selective detector (MSD) was used for compound identification and quantification. The purge and trap method consisted of the following cycle: four minute dry purge, preheat to 175 °C, and desorb at 180 °C for 2.75 minutes. The GC operation consisted of the following temperature program: starting temperature of 24 °C, ramp to 42 °C at 30 °C/min, hold at 42 °C for 2.33 minutes, ramp to 175 °C at 11 °C/min, ramp to 210 °C at 30 °C/min, and final hold at 210 °C for 2 minutes. Three-point external calibration curves were completed and used for quantifying CDC13 and EDB mass on adsorbent tubes.

## EXPERIMENTAL RESULTS

### Oxygen Transfer Experiments

Results of oxygen mass transfer experiments were used to calculate values of  $K_s$  based on Equation 14. Figures 3 through 5 show  $K_s$  versus drop height (h) for three different wastewater flow conditions. A best-fit regression line, and resulting linear regression equation, is included in each figure. The  $R^2$  values ranged from 0.79 to 0.98, indicating a strong correlation between drop height and oxygen transfer.

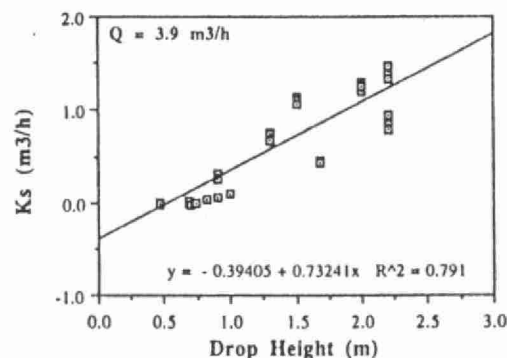


FIGURE 3. Lumped oxygen transfer coefficient versus drop height for low flow conditions.

For each wastewater flow range,  $K_s$  increased with increased drop height. This makes intuitive sense in terms of each of the mass transfer mechanisms illustrated in Figure 1. An increase in drop height should correspond to a) an increase in free-fall time and effective interfacial surface area, b) an increase in splashing and airborne droplets following impact with the

underlying tailwater, c) an increase in the agitation of the tailwater, consistent with increased turbulent kinetic energy and tailwater surface renewal, and d) increased entrained air volume.

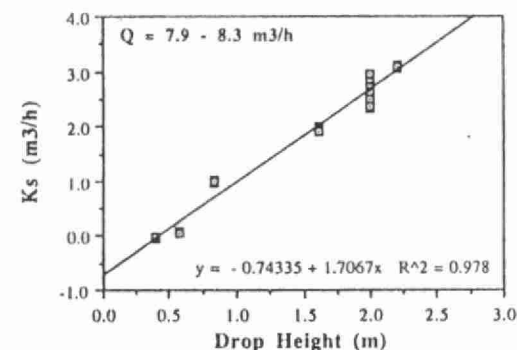


FIGURE 4. Lumped oxygen transfer coefficient versus drop height for mid flow conditions.

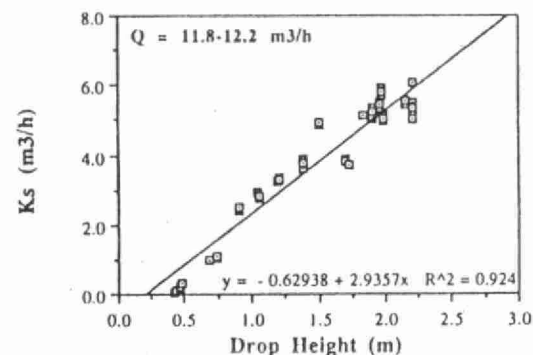


FIGURE 5. Lumped oxygen transfer coefficient versus drop height for high flow conditions.

Between Figures 3 through 5, the mass transfer coefficient becomes more sensitive to drop height (increased slope of regression line) as wastewater flow rate ( $Q$ ) increases from  $3.9 \text{ m}^3/\text{hr}$  to approximately  $12 \text{ m}^3/\text{hr}$ . The effect of wastewater flow rate on oxygen mass transfer is illustrated in Figures 6 and 7, in which  $K_s$  is plotted versus  $Q$  with drop height ( $h$ ) and tailwater depth ( $z$ ) held constant. For both of the fixed ( $h, z$ ) combinations, a strong correlation ( $R^2 = 0.98$ ) was observed between mass transfer and  $Q$ . Furthermore, the effects of ( $h, z$ ) combinations on the

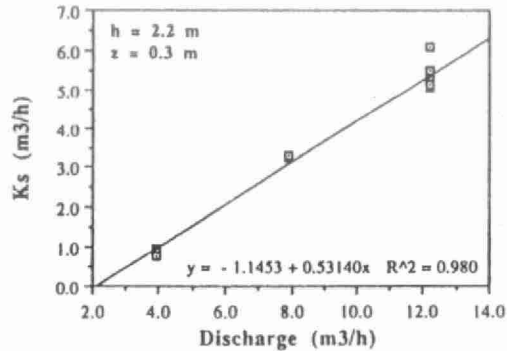


FIGURE 6. Lumped oxygen transfer coefficient versus wastewater discharge (drop height and tailwater depth fixed at 2.2 m and 0.3 m, respectively).

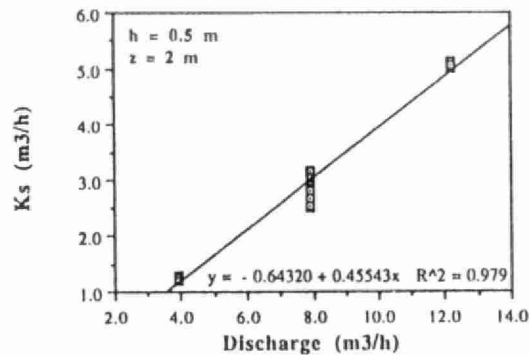


FIGURE 7. Lumped oxygen transfer coefficient versus wastewater discharge (drop height and tailwater depth fixed at 0.5 m and 2.0 m, respectively).

sensitivity of  $K_s$  to  $Q$  was very small, suggesting similarities in the mechanisms that cause mass transfer in either case. Given the difference in falling wastewater area for each ( $h, z$ ) combination, it is likely that mass transfer to the falling wastewater is not a significant mechanism relative to tailwater agitation/splashing and air entrainment.

While oxygen mass transfer is very sensitive and directly proportional to drop height and wastewater discharge, its sensitivity to tailwater depth is much different. The data plotted in Figures 3 through 5 show  $K_s$  versus drop height at approximately constant flow rates, but independent of tailwater depth. Best-fit linear regression equations are provided for each flow condition, separated by three categories of tailwater depth, in Table I. These equations do not indicate a strong trend between  $K_s$  and tailwater depth for the conditions tested in this study.

TABLE I. Best-fit linear regression equations for  $K_s$  as a function of drop height.

Condition	Equation	Number of data points	$R^2$
Low flow			
• all data	$K_s = 0.73h - 0.39$	51	0.79
• low tailwater	$K_s = 0.60h - 0.13$	18	0.58
• mid tailwater	$K_s = 0.95h - 0.60$	20	0.98
• high tailwater	$K_s = 0.37h - 0.21$	13	0.96
Mid flow			
• all data	$K_s = 1.71h - 0.74$	30	0.98
• low tailwater	$K_s = 1.64h - 0.32$	8	1.00 <sup>a</sup>
• mid tailwater	NA	7	NA
• high tailwater	$K_s = 1.70h - 0.82$	15	0.99
High flow			
• all data	$K_s = 2.94h - 0.63$	58	0.92
• low tailwater	$K_s = 2.25h + 0.43$	17	0.96
• mid tailwater	$K_s = 3.38h - 1.28$	14	0.93
• high tailwater	$K_s = 3.22h - 0.98$	15	0.87

UNITS: In the equations listed above,  $K_s$  has units of  $\text{m}^3/\text{hr}$  and drop height ( $h$ ) has units of m.

Low flow:  $3.9 \text{ m}^3/\text{hr}$

Mid flow:  $7.9$  to  $8.3 \text{ m}^3/\text{hr}$

High flow:  $11.8$  to  $12.2 \text{ m}^3/\text{hr}$

Low tailwater:  $0.30$  to  $0.40 \text{ m}$

Mid tailwater:  $0.50$  to  $0.60 \text{ m}$

High tailwater:  $0.70$  to  $1.0 \text{ m}$

a: For mid flow and low tailwater depth, all data clustered at only two drop heights.

NA: For mid flow and mid tailwater, all data clustered at one drop height.

## Volatile Tracer Experiments

The results of preliminary deuterated chloroform (CDCI<sub>3</sub>) and ethylene dibromide (EDB) tracer experiments are presented in Table II. With the exception of a higher wastewater flow rate during experiment 2, all operating conditions and sampling procedures were the same between each experiment. For each experiment, gas samples were collected well before steady-state conditions were reached. Thus, with little gas accumulation in the PDS head space, the experimental system approached an open drop structure. Therefore, it was not possible to correctly apply the steady-state LSM and AEM equations described previously for back-calculation of  $K_s$  or  $Q_e$ . Experiments are continuing using the same pilot drop structure described previously to assess  $K_s$  and  $Q_e$  under steady-state conditions and a range of system operating parameters.

For each tracer experiment, average percent stripped values were calculated based entirely on influent mass loading and losses from the liquid phase. These results are provided in Table II, and indicate a greater stripping efficiency for CDCI<sub>3</sub> than EDB during each of the two experiments. This is consistent with the higher volatility, in terms of Henry's law constant, of CDCI<sub>3</sub> than EDB. The stripping efficiencies ranged from 20% for EDB (experiment 2) to 40% for CDCI<sub>3</sub> during experiment 1. In a companion paper it has been suggested that the length of uniform reaches necessary to achieve 50% VOC removal by volatilization under many practical sewer operating conditions can exceed 10 to 100 km. Therefore, drop structures such as drop manholes and drops into pump station wet wells are likely to be significant contributors to overall VOC and semi-VOC emissions from sewers.

TABLE II. Results of CDCI<sub>3</sub> and EDB tracer experiments.

Condition/parameter	Experiment 1	Experiment 2
Fall height (m)	2.0	2.0
Tailwater depth (m)	0.5	0.5
Wastewater discharge (m <sup>3</sup> /hr)	9.0	13.9
Headspace ventilation rate (m <sup>3</sup> /hr)	4.6	4.6
Wastewater temperature (°C)	20	20
$K_s$ (oxygen) (m <sup>3</sup> /hr)	3.9	5.9
Average % Stripped:		
• CDCI <sub>3</sub>	40	27
• EDB	24	20

Although the wastewater flow rate and oxygen mass transfer coefficients were greater for experiment 2 than experiment 1, the opposite was true for the fraction stripped for both tracer compounds. It is difficult to ascertain the significance of this result based on the limited number of experiments which have been completed to date. Thus, future experiments are planned under similar PDS operating conditions.

## SUMMARY AND CONCLUSIONS

There have been a few previous studies of gas-liquid mass transfer at drop structures. However, these studies have generally focussed on oxygen absorption under clean water conditions. There is very little published literature on oxygen transfer to untreated wastewater, and a paucity of information related to VOC stripping from wastewater drop structures. This paper provided a review of the major mechanisms likely to cause mass transfer of VOCs and semi-VOCs at drop structures in sewers. Four estimation methods and their limitations were described. Results of a complete set of pilot oxygen transfer experiments and preliminary pilot VOC/semi-VOC experiments were presented.

The oxygen results presented in this paper suggest strong correlations between oxygen mass transfer and both drop height and wastewater flow rate. In each case, oxygen transfer coefficients increased approximately linearly with increases in drop height or discharge, when the other parameter was held constant. Oxygen mass transfer was not significantly influenced by changes in tailwater depth for the conditions which were studied.

Preliminary volatile tracer experiments suggest that sewer drop structures may be significant contributors to overall semi-VOC and VOC emissions from sewers. However, additional experiments are necessary to ascertain the relative significance of individual mass transfer mechanisms, and to evaluate several parameters required for the application of mechanistic models of emissions from drop structures. A series of drop structure/VOC tracer experiments is currently underway at the Wastewater Technology Centre in Burlington, Ontario.

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# **VOC Emissions from Industrial Sewers: An Improved Estimation Method Based on Oxygen Transfer Potential**

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## INTRODUCTION

As a result of the CAA of 1990, several industries have come under increased regulatory scrutiny as sources of hazardous air pollutant (HAP) emissions. For example, over the next several years the Environmental Protection Agency (EPA) has been mandated to propose and promulgate National Emission Standards for Hazardous Air Pollutants (NESHAPs) for 189 HAPs emitted from 174 industrial source categories. Many of the listed HAPs can be classified as volatile organic compounds (VOCs). One source that has received significant attention is on-site industrial sewers, particularly HAP emissions associated with process drains and drop structures.

An understanding of the extent and nature of gas-liquid mass transfer within industrial sewers is of fundamental importance for:

1. identifying the need and criteria for source-specific NESHAPs control requirements, and
2. determining the feasibility of HAP emissions suppression by reducing gas-liquid mass transfer through minor process modifications.

The latter would be facilitated by the existence of mathematical models to predict HAP emissions based on process operating conditions and compound physicochemical properties. Unfortunately, existing knowledge and published information related to HAP emissions from industrial sewers is very limited, making it difficult to accurately estimate source-specific emissions potential and/or the potential for emissions suppression. The high uncertainties associated with HAP emissions estimates for on-site industrial sewers may lead to significant errors (under or overestimation) regarding the benefits of source-specific NESHAPs and subsequent control requirements.

Industry-specific NESHAPs compliance options are intended to provide flexibility, but will require controls that can achieve similar or greater HAP reductions in comparison with a reference control technology. Alternate control options might include source reduction, steam stripping with gas-phase control at point of origin, and steam stripping with gas-phase control at the effluent of an on-site sewer. The latter might require hard-piping of a sewer system or sealing the system to minimize volatile losses. Furthermore, sealing of a system requires an assessment of explosion hazards, with possible blanketing using an inert gas. For biodegradable HAPs, there is also potential for suppression of gas-liquid mass transfer in existing sewers, with subsequent "enhanced" liquid-phase treatment within on-site biological reactors. Such an alternative is attractive with respect to reduced capital and operating costs for HAP control.

The potential for improvements in predicting HAP emission potentials from industrial sewers is the focus of this paper. A method for relating oxygen transfer measurements or estimates and stripping of volatile HAPs at drop structures is presented. Pilot and field experiments are described, with results serving the purpose of model evaluation. The information presented in this paper should be useful for individuals involved with emission inventories, development of NESHAPs for wastewater collection systems, and investigations of HAP control using process modifications.

## BACKGROUND

Gas-liquid mass transfer of VOCs and semi-VOCs can be classified as occurring at two general locations in sewers: 1) along relatively-uniform flow reaches, e.g. interceptor channels, and 2) at points of rapid dissipation of potential energy, e.g. drop manholes or free-fall drops into pump station wet wells.<sup>1-2</sup> Studies which have focussed on VOC emissions from sewers have indicated that, with some exceptions,

removal by stripping along 1 to 5 km stretches of relatively uniform sewer channels is small, i.e. less than 10%.<sup>3</sup> However, there is little information to suggest the relative importance of VOC emissions from small sewer drop structures, e.g. drops into pump station wet wells or drop manholes.

Several mechanisms can contribute to gas-liquid mass transfer at sewer drop structures. Mass transfer can occur at

- the free-falling wastewater surface
- splashing and airborne droplets generated at the tailwater surface
- agitated tailwater surface
- air bubbles entrained in the tailwater.

However, experimental separation of these mechanisms is complex at best, and methods to predict the contribution of each mechanism have not been reported. For these reasons, existing models of mass transfer at drop structures are empirical.<sup>4-6</sup>

### Relating Oxygen and VOC Mass Transfer

There has been significant interest in the possible use of inexpensive, routine oxygen transfer measurements or estimates as a surrogate for VOC emissions potential at hydraulic structures. Oxygen transfer at water and wastewater drop structures is typically defined in terms of dissolved oxygen concentrations relative to an equilibrium state upstream and downstream of a drop (oxygen deficit ratio):

$$r_o = \frac{C_{1o} - \frac{C_{go}}{H_{co}}}{C_{2o} - \frac{C_{go}}{H_{co}}} \quad (1)$$

where

- $r_o$  = oxygen deficit ratio
- $C_{1o}$  = dissolved oxygen concentration upstream of a drop structure in  $\text{mg}/\text{m}^3$
- $C_{2o}$  = dissolved oxygen concentration downstream of a drop structure in  $\text{mg}/\text{m}^3$
- $C_{go}$  = gaseous oxygen concentration in a drop structure headspace in  $\text{mg}/\text{m}^3$
- $H_{co}$  = Henry's law coefficient for oxygen in  $\text{m}^3\text{liq} / \text{m}^3\text{gas}$ .

A similar relationship can be defined as the deficit ratio for a specific VOC:

$$r_v = \frac{C_1 - \frac{C_g}{H_c}}{C_2 - \frac{C_g}{H_c}} \quad (2)$$

where

- $C_1$  = VOC concentration in liquid immediately upstream of a drop structure in  $\text{mg}/\text{m}^3$
- $C_2$  = VOC concentration in liquid immediately downstream of a drop structure in  $\text{mg}/\text{m}^3$
- $C_g$  = gaseous VOC concentration in drop structure headspace in  $\text{mg}/\text{m}^3$
- $H_c$  = Henry's law coefficient for a specific VOC in  $\text{m}^3\text{liq} / \text{m}^3\text{gas}$ .

In the past, researchers have related oxygen and VOC deficit ratios according to:<sup>7-8</sup>

$$r_v = r_o^\Psi \quad (3)$$

$$\psi = \left\{ \frac{D_v}{D_o} \right\}^n \quad (4)$$

where

$$\begin{aligned} D_v &= \text{liquid-phase molecular diffusion coefficient of a VOC in m}^2/\text{hr} \\ D_o &= \text{liquid-phase molecular diffusion coefficient for oxygen in m}^2/\text{hr} \\ n &= \text{diffusivity-adjustment exponent.} \end{aligned}$$

The value of  $n$  in Equation 4 varies from 0.5 (penetration and surface renewal theories) to 1.0 (two-film theory).<sup>9-10</sup>

For systems that are open to the atmosphere or that are characterized by high rates of headspace ventilation, gas-phase accumulation above a drop structure can be neglected and VOC stripping efficiency ( $\xi$ ) can be estimated as

$$\xi = 1 - \frac{1}{r_v} \quad (5)$$

Otherwise, a mass balance on the gas-phase is necessary to account for mass transfer retardation by gaseous VOC accumulation. Resulting equations for such a condition have been reported elsewhere<sup>7</sup> and will not be considered further in this paper.

A limitation of Equations 3 and 4 is that they are based on implicit assumptions that 1) gas-phase resistance to mass transfer is negligible relative to liquid-phase resistance for both oxygen and a VOC of interest, and 2) mass transfer limitations caused by accumulation of a VOC in entrained air do not significantly affect overall mass transfer. The first assumption is generally believed to be valid for oxygen. However, gas-phase resistance to mass transfer may be significant for some VOCs, depending on their physicochemical properties and the degree of air entrainment at drop structures. For a wide range of semi-VOCs and VOCs, Hsieh *et al.*<sup>11</sup> reported gas-to-liquid film mass transfer coefficients for diffused bubbles that were significantly lower than those for other air-water systems. The second assumption may not be valid for many drop structures and VOCs, particularly for those with lower Henry's law coefficients, i.e. compounds that may approach equilibrium rapidly in diffused bubbles.

To account for gas-phase limitations to mass transfer, Equations 3 and 4 can be modified to yield:

$$r_v = r_o \Psi \quad (6)$$

where

$$\Psi = \frac{\psi}{1 + \frac{1}{H_c B}} \quad (7)$$

The term  $B$  in Equation 7 is a parameter that accounts for mass transfer retardation due to gas accumulation in entrained air bubbles, as well as gas-phase resistance to mass transfer. If the latter is assumed to dominate, term  $B$  becomes simply the ratio of gas-to-liquid phase mass transfer coefficients in accordance with two-film theory.

Hsieh *et al.*<sup>11</sup> completed laboratory experiments to determine values of  $\Psi$  for diffused bubble aeration and a wide range of semi-volatile and volatile organic compounds. For this study, Hsieh *et al.*'s data were used to determine the following empirical relationship between  $\Psi$  and  $H_c$ :

$$\Psi = 0.15 \ln(H_C) + 0.49. \quad (8)$$

The  $R^2$  value for Equation 8 was 0.995. The applicability of Equation 8 is limited to compounds with  $H_C > 0.04 \text{ m}^3_{\text{liq}} / \text{m}^3_{\text{gas}}$ . For less volatile compounds, the empirical nature of Equation 8 leads to negative values of  $\Psi$ .

Based on Equations 5 through 7, it should be possible to accurately estimate VOC emissions at drop structures given appropriate values of  $r_0$ ,  $H_C$  and  $\Psi$  (or  $B$ ). It should, however, be noted that dilute aqueous solutions are assumed, and industrial wastewaters with high ionic strength, significant levels of surfactants, high concentrations of dissolved non-volatile organics, or immiscible organic phases pose complications beyond the scope of this study.

Values of  $H_C$  have been reported for most VOCs of interest, and can be estimated for many VOCs using relationships reported by Ashworth *et al.*<sup>12</sup> and Gossett<sup>13</sup>. Values of  $\Psi$  can be estimated using Equation 8, particularly for drop structures in which air entrainment dominates other mass transfer mechanisms. For a particular system,  $r_0$  can be obtained through actual measurements of dissolved oxygen immediately upstream and downstream of a drop structure, and oxygen concentrations above the drop, i.e. ambient air for open systems or a confined headspace for closed systems. If measured  $r_0$  values are not available, they can be estimated using empirical models reported in the literature.<sup>4-6</sup> Multi-variable models afford an opportunity to estimate the effects of process operating conditions on VOC emissions from drop structures. For example, Nakasone<sup>6</sup> presented a model for  $r_0$  that accounts for variations in liquid flowrate, drop height, and tailwater depth at weirs.

## METHODOLOGY

For this study, VOC stripping efficiencies were determined based on five pilot experiments and one field monitoring event in a large municipal sewer consisting of several large drop structures in series. Results of pilot and field experiments were compared with stripping efficiencies estimated based on Equations 5 through 8. For all experiments, values of  $r_0$  were estimated based on a model by Nakasone.<sup>6</sup> For most of the VOCs which were studied, values of  $H_C$  were estimated as a function of water temperature using Ashworth *et al.*<sup>12</sup> and Gossett<sup>13</sup>. Otherwise, compound-specific solubility and vapor pressure data were used to estimate  $H_C$ . Pilot and field experimental methodologies are described below.

### Pilot Experiments

A pilot-scale drop structure was constructed at the Wastewater Technology Centre (WTC) in Burlington, Ontario. An illustration of the experimental system is provided in Figure 1. The system consisted of four major components: tracer injection system, enclosed drop chamber, headspace ventilation system, and sample collection system. Each of these components is described below. Additional details regarding the experimental system have been reported elsewhere.<sup>2</sup>

Volatile tracers were stored in a 25 L glass carboy. The tracer solution was prepared as 1:5 parts methanol in tap water to enhance tracer solubility and to minimize volatile losses during storage. The tracer reservoir was always prepared immediately prior to each pilot experiment, with tracer concentrations maintained at less than 10% of solubility in clean water for each compound. Quality assurance testing indicated that negligible quantities of tracer were lost during the course of each experiment, i.e. by analyzing tracer concentrations based on samples collected from the tracer reservoir prior to and immediately following an experiment. The tracer solution was injected immediately upstream of a static mixer through a 6 mm i.d. stainless-steel tube extending into a pressurized clean (tap) water stream. Following the static mixer, the water/tracer solution was pumped to an enclosed gravity-flow entrance pipe (PVC) connected to the drop chamber.

The chamber consisted of a cylindrical, fiberglass tank with a height of 3.0 m and an internal diameter of 1.2 m. Water flowed into the chamber, flowed over a drop, and accumulated in the base (tailwater) of the chamber before exiting to a floor drain. Tailwater depth was controlled through vertical adjustments of a flexible hose attached to the effluent pipe. Three flanges of 15 cm i.d. were staggered around the perimeter of the chamber at heights of 1.2 m, 1.8 m, and 2.5 m, measured as the distance from an entry pipe invert to the chamber floor. An influent pipe could be connected to any of these entrances to maintain a constant drop height. The other entries were sealed when not in use.

For this study, it was desired to minimize the retardation of mass transfer caused by tracer accumulation in the chamber headspace. Thus, for four of the five pilot experiments, compressed air was supplied to the drop chamber headspace at rates ranging from 16 to 40 m<sup>3</sup>/h, and all tracers were characterized as having  $H_c > 0.14 \text{ m}^3_{\text{liq}} / \text{m}^3_{\text{gas}}$  at experimental water temperatures. The third experiment was intentionally completed with a lower headspace ventilation rate of 8 m<sup>3</sup>/h to confirm mass transfer retardation. For each experiment, flowrate was regulated using a rotameter upstream of air entry into the drop chamber headspace (at a height of 1.8 m above the chamber floor). Air flowrates were verified using a hot-wire anemometer which was inserted into the drop chamber exhaust vent. Subsequent gas and liquid sampling confirmed that, for experiments with gas flowrates greater than 16 m<sup>3</sup>/h, the system was far from equilibrium as defined by Henry's law, i.e. it could effectively be considered an open system for all volatile tracers.

Four of the six experiments were completed using a tracer cocktail containing six target VOCs, including 1,3,5-trimethylbenzene, toluene, o-xylene, trichloroethene, tetrachloroethene, and 1,1,1-trichloroethane. Tetrachloroethene was not analyzed for the second and third experiments. During the start of each experiment, desired water flowrate, tailwater depth, and headspace ventilation rates were established and recorded. Following the collection of background samples, tracer injection was initiated at a pre-set injection rate (usually 40 ml/min), and initial injection time was recorded. The system was then allowed to reach a steady-state condition during a time period corresponding to a minimum of 3.5 hydraulic/aerodynamic residence times of the tailwater pool and chamber headspace.

The experimental system consisted of three sampling locations: 1) a liquid sample valve immediately upstream of water entry into the drop chamber, 2) a liquid sample riser pipe located immediately downstream of water discharge from the drop chamber, and 3) a gas sample port on the exhaust vent. At steady-state, two sequential liquid samples were collected upstream and downstream of the drop chamber. All liquid samples were collected with zero headspace in thermally-conditioned 40 ml amber vials with teflon®-lined screw caps. A steady-state gas sample was also collected from the exhaust vent sample port during each experiment. Gas samples were collected using pre-conditioned and evacuated stainless steel canisters.

Experimental conditions for each of the five pilot experiments are listed in Table 1.

### Field Experiments

The field site selected for study was a large sewer interceptor (Massey Creek Interceptor: MCI) located in metropolitan Toronto, Ontario. Previous monitoring of the MCI indicated continuous weekday occurrences of several VOCs at high concentrations, some greater than 1 mg/L in liquid.<sup>14</sup> Thus, the use of surrogate tracers was not required during the field experiment. In-system VOCs which were used as "tracers" for this study included ethylbenzene, o-xylene, m,p-xylenes, toluene, tetrachloroethene, 1,3,5-trimethylbenzene, propylbenzene, 1,3-diethylbenzene and 1,4-diethylbenzene. A schematic of the MCI is presented in Figure 2. Physical characteristics of the reach included a total length of 1.6 km, channel slopes ranging from 0.25 to 1.0%, pipe diameters ranging from 0.9 m to 1.2 m, 17 manholes (14 with highly perforated covers), and four drops ranging from 0.15 to 3.0 m in height. Distances, channel

slopes and pipe diameters between any two manholes are listed in Figure 2. Flowing at half-full in the 0.25% channel slope section, the MCI conveyed wastewater at a rate of approximately  $0.4 \text{ m}^3/\text{s}$ . For this study, the mid-day flowrate was  $0.2 \text{ m}^3/\text{s}$ , with a depth of approximately 20 cm. Wastewater temperature was  $16^\circ\text{C}$ .

A preliminary reach inspection was performed and indicated that the downstream section of the interceptor bounded by manholes 7 and 31 (MH7 and MH31) contained the manholes through which the majority of natural outgassing occurred. This is depicted in Figure 2 by vertical arrows. In this section there were five highly perforated outgassing manhole covers, each containing 66 pickholes. Outgassing flowrates from individual manhole covers were monitored using a hot wire anemometer. Flowrates across the five perforated manhole covers generally ranged from between 1300 and 2300  $\text{m}^3/\text{h}$  during mid-day conditions. Total gaseous flowrates and flow direction were confirmed using sulfur hexafluoride tracing and dilution. It was observed that headspace ventilation occurred in the direction of wastewater flow, with principal outgassing between MH7 and MH31. Tracer analyses confirmed anemometer measurements of gas flowrate to within 15%. The MCI headspace was sufficiently well-ventilated to maintain the system far from equilibrium for all VOCs that were analyzed.

Wastewater sample collection was performed on a weekday between 14:00 and 16:00 hours to determine VOC stripping efficiencies from MH9 to MH6, i.e. across two large drop structures. Wastewater grab samples were collected at two locations along the MCI: MH6 and MH9. Starting at 14:00 hours at each manhole, samples were collected approximately every ten minutes for 100 minutes. Three gas samples were collected in the MCI headspace at MH6 in accordance with the methods described above for pilot experiments.

Wastewater samples were drawn from the MCI to ground level through weighted, submerged 6 mm o.d. teflon® tubing. Continuous wastewater transport was performed by peristaltic pumps driven by portable generators. Grab samples were collected in 40 mL EPA-certified amber glass vials. Each sample was filled to capacity ensuring zero headspace and then sealed with teflon®-lined screw caps. Wastewater samples were stored in an ice chest while in the field.

Wastewater flowrate measurements were obtained through the use of an existing flowmeter stationed at MH3 and maintained by the Metropolitan Works Department of Toronto. Flowrates were recorded every 20 minutes.

#### Sample Analysis

Each liquid sample which was collected during pilot experiments was analyzed separately. Variabilities in concentration between steady-state liquid samples collected at the same location were consistently less than 10%. Thus, for purposes of analysis, steady-state concentrations of each tracer were averaged. Liquid samples which were collected during field experiments were composited prior to analysis. All liquid samples were analyzed using EPA method 624. All gas samples were analyzed using EPA method TO-14.

## RESULTS AND DISCUSSION

Compound-specific stripping efficiencies (measured) and ratios of predicted-to-measured stripping efficiencies are listed in Table 2 for all experiments. Average mass closure over all pilot experiments was 95%, with the worst being 87% for 1,3,5-trimethylbenzene during pilot experiment 1 (pilot #1). Average mass closures were 98% for pilot #4 and pilot #5.

Pilot experiments 1 through 3 were completed under nearly identical conditions, with the only difference being headspace ventilation as listed in Table 1. For each experiment, there was little variation in



measured stripping efficiencies for the three tracers with similar values of  $H_c$  (1,3,5-trimethylbenzene, toluene, and o-xylene). Stripping efficiencies consistently increased with increasing  $H_c$  and, with the exception of 1,1,1-trichloroethane, were similar for pilot experiments 1 and 2. The greatest differences were observed for the most volatile tracers, trichloroethene and 1,1,1-trichloroethane, with stripping efficiencies greater during pilot #1 (higher headspace ventilation rate). For all tracers, measured stripping efficiencies were lower during pilot #3 (lowest headspace ventilation rate) than either of pilot #1 or pilot #2. This trend suggests that less ventilation during pilot #3 lead to enough gaseous VOC accumulation to retard overall mass transfer from liquid to gas. The importance of the product of headspace ventilation rate and Henry's law coefficient has been described elsewhere.<sup>2</sup>

For 10 of 11 compounds during pilot #1 and pilot #2, the relative difference between predicted and measured stripping efficiencies was less than 12%, well within experimental error. The exception was 1,1,1-trichloroethane during pilot #1 (predicted 33% lower than measured). The average ratios of predicted-to-measured stripping efficiencies for pilot #1 and pilot #2 were 0.96 and 1.0, respectively. However, for pilot #3 the average ratio of predicted-to-measured stripping efficiencies was 1.48, which indicates the importance of accounting for retardation of mass transfer by gas-phase accumulation in a sewer headspace.

Pilot #4 and pilot #5 were completed at different water temperatures and flowrates, and with significantly lower drop heights than pilot experiments 1 through 3. For each experiment, measured stripping efficiencies were consistently between 3 and 5%, much lower than those measured for pilot #1-3. These results clearly illustrate the importance of accounting for differences in system operating conditions and compound properties when estimating volatile HAP emissions from sewers. The sensitivity of stripping efficiency to  $H_c$  was lower for pilot #4 and pilot #5 than for pilot #1-3. This suggests that air entrainment is a less significant mass transfer mechanism for low drop height conditions. Finally, predicted stripping efficiencies generally underestimated measured stripping efficiencies for pilot #4 and pilot #5. The average ratios of predicted-to-measured stripping efficiencies were 0.53 and 0.82 for pilot #4 and pilot #5, respectively.

Field experimental conditions differed from pilot experimental conditions in many ways. For example, wastewater flowrate during the field experiment was nearly 200 times the water flowrate used during pilot #1-3. The field experiment was completed in a sewer containing municipal wastewater characterized by significant quantities of VOC-laden industrial discharge. All pilot experiments were completed with potable drinking water. Pilot experiments were completed using single drops with heights varying from 0.4 to 1.7 m. Field experiments were completed in a segment of sewer containing two drop structures with drop heights of 3.0 and 1.4 m. Thus, an overall VOC deficit ratio was based on the product of two deficit ratios in series.

Measured stripping efficiencies during field experiments ranged from 25 to 38%, underscoring the fact that significant quantities of volatile HAPs may be removed from wastewater prior to reaching a downstream treatment facility. Again, measured VOC stripping efficiencies generally increased with increasing values of  $H_c$ , suggesting the importance of air entrainment as a mass transfer mechanism. The average ratio of predicted-to-measured stripping efficiencies was 0.99, and the relative difference between measured and predicted values were generally well within experimental error.

Predicted VOC stripping efficiencies are plotted versus measured stripping efficiencies over all experiments in Figure 3. A 1:1 line which closely resembles a best linear fit is included in Figure 3. The linear best-fit equation through all data was determined to be:

$$(\text{stripping efficiency})_{\text{predicted}} = 1.02 (\text{stripping efficiency})_{\text{measured}} - 0.29 \quad (9)$$

The  $R^2$  value associated with Equation 9 was 0.95. This, as well as other results described above, suggest that there is significant potential for using adjusted oxygen transfer predictions to estimate volatile HAP stripping efficiencies from sewers.

Finally, the results described in this paper were based entirely on predicted oxygen deficit ratios. Future experiments will be completed to assess whether differences in predicted and measured VOC stripping efficiencies can be improved through the use of measured oxygen deficit ratios.

## SUMMARY AND CONCLUSIONS

Improvements in the ability to estimate emissions of volatile HAPs from industrial and municipal sewers are needed to facilitate rational development of regulations to control such emissions, and to allow industry and municipalities to develop appropriate strategies for effectively reducing such emissions. Pilot and field experiments were completed to assess the potential for using oxygen deficit ratios to estimate VOC stripping efficiencies from sewer drop structures. Experimental procedures and results were described in this paper. Major findings and conclusions include:

- 1) Stripping efficiencies for volatile HAPs is a complex function of many system operating conditions and chemical properties. Therefore, emissions estimates based on simple stripping or emission factors are likely characterized by significant uncertainty.
- 2) Under appropriate conditions, significant quantities of volatile HAPs may be removed from sewers prior to wastewater reaching a downstream treatment facility. This is particularly true in well-ventilated sewers characterized by more than one large drop structure.
- 3) Results associated with the use of oxygen deficit predictions to estimate volatile HAP stripping efficiencies are promising, and should be pursued further. Future research should be completed in operating industrial sewers, and should be extended to measured as well as predicted oxygen deficit ratios.

The authors hope that the results described in this paper will be useful for future studies aimed at improving VOC emissions estimates from industrial and municipal sewers, and that the final outcome is a set of working tools that will be of value to regulators, as well as staff of industries and municipalities.

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Table 1. Pilot experimental operating conditions.

Expt	Water Temperature (°C)	Flowrate (m <sup>3</sup> /h)		Drop Height (m)	Tailwater Depth (m)
		Liquid	Gas		
1	12	4	21	1.7	0.5
2	12	4	16	1.7	0.5
3	12	4	8	1.7	0.5
4	5.5	8	40	0.4	0.5
5	5.5	12	40	0.4	0.5

Table 2. Compound-specific stripping efficiencies for pilot and field experiments.

Expt	Compound	$H_c^a$	Measured % stripped	Predicted/ Measured
1	1,3,5-trimethylbenzene	0.18	8	1.08
	toluene	0.18	9	0.97
	o-xylene	0.19	8	1.10
	trichloroethene	0.25	11	1.03
	tetrachloroethene	0.40	15	0.88
	1,1,1-trichloroethane	0.44	21	0.67
2	1,3,5-trimethylbenzene	0.18	10	0.91
	toluene	0.18	9	0.96
	o-xylene	0.19	9	1.06
	trichloroethene	0.25	11	1.01
	1,1,1-trichloroethane	0.44	13	1.04
3	1,3,5-trimethylbenzene	0.18	6	1.45
	toluene	0.18	6	1.50
	o-xylene	0.19	6	1.64
	trichloroethene	0.25	8	1.41
	1,1,1-trichloroethane	0.44	10	1.39
4	1,3,5-trimethylbenzene	0.14	4	0.51
	toluene	0.14	4	0.50
	o-xylene	0.15	4	0.57
	trichloroethene	0.19	4	0.49
	tetrachloroethene	0.29	5	0.55
	1,1,1-trichloroethane	0.35	5	0.57
5	1,3,5-trimethylbenzene	0.14	3	0.61
	toluene	0.14	4	0.86
	o-xylene	0.15	3	1.00
	trichloroethene	0.19	4	0.83
	tetrachloroethene	0.29	5	0.77
	1,1,1-trichloroethane	0.35	5	0.85
Field	1,3-diethylbenzene	0.17	25	1.12
	1,4-diethylbenzene	0.17	25	1.12
	toluene	0.20	30	1.00
	ethylbenzene	0.20	31	0.97
	1,3,5-trimethylbenzene	0.21	33	0.94
	m,p-xylene	0.22	32	0.97
	propylbenzene	0.31	38	0.95
	tetrachloroethene	0.49	36	0.84

a. Henry's law coefficient with units of  $m_{liq}^1/m_{gas}^1$

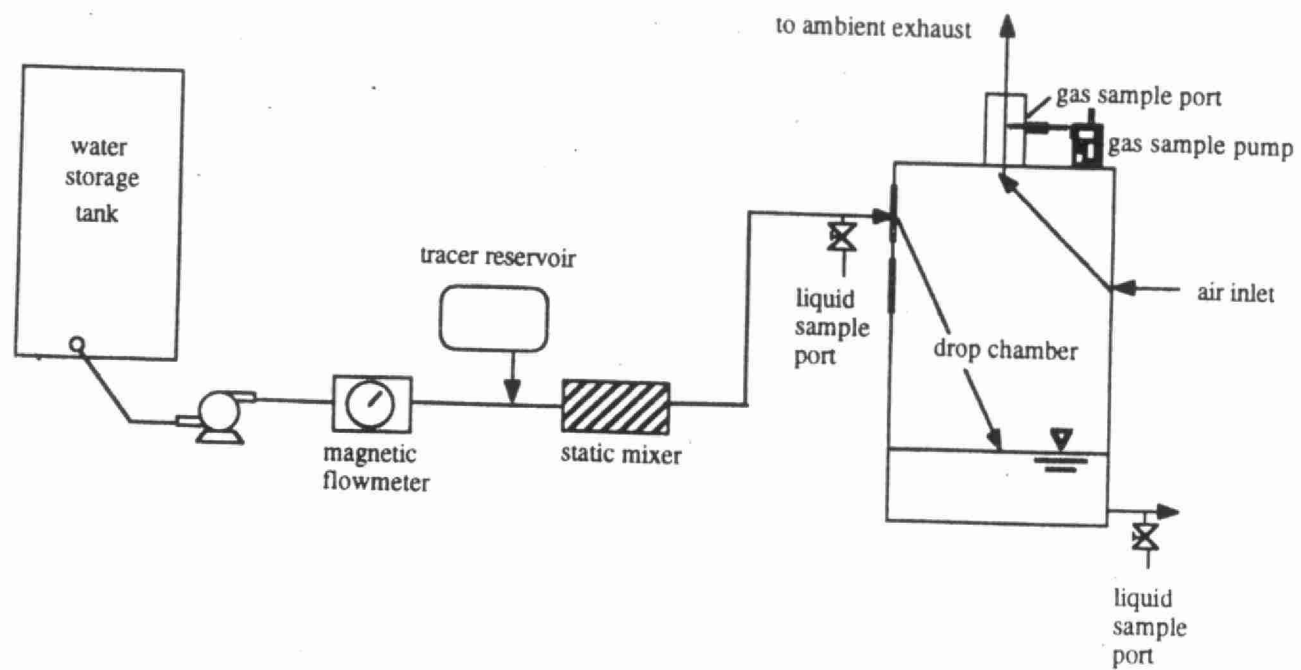


Figure 1. Major components of pilot experimental drop structure.

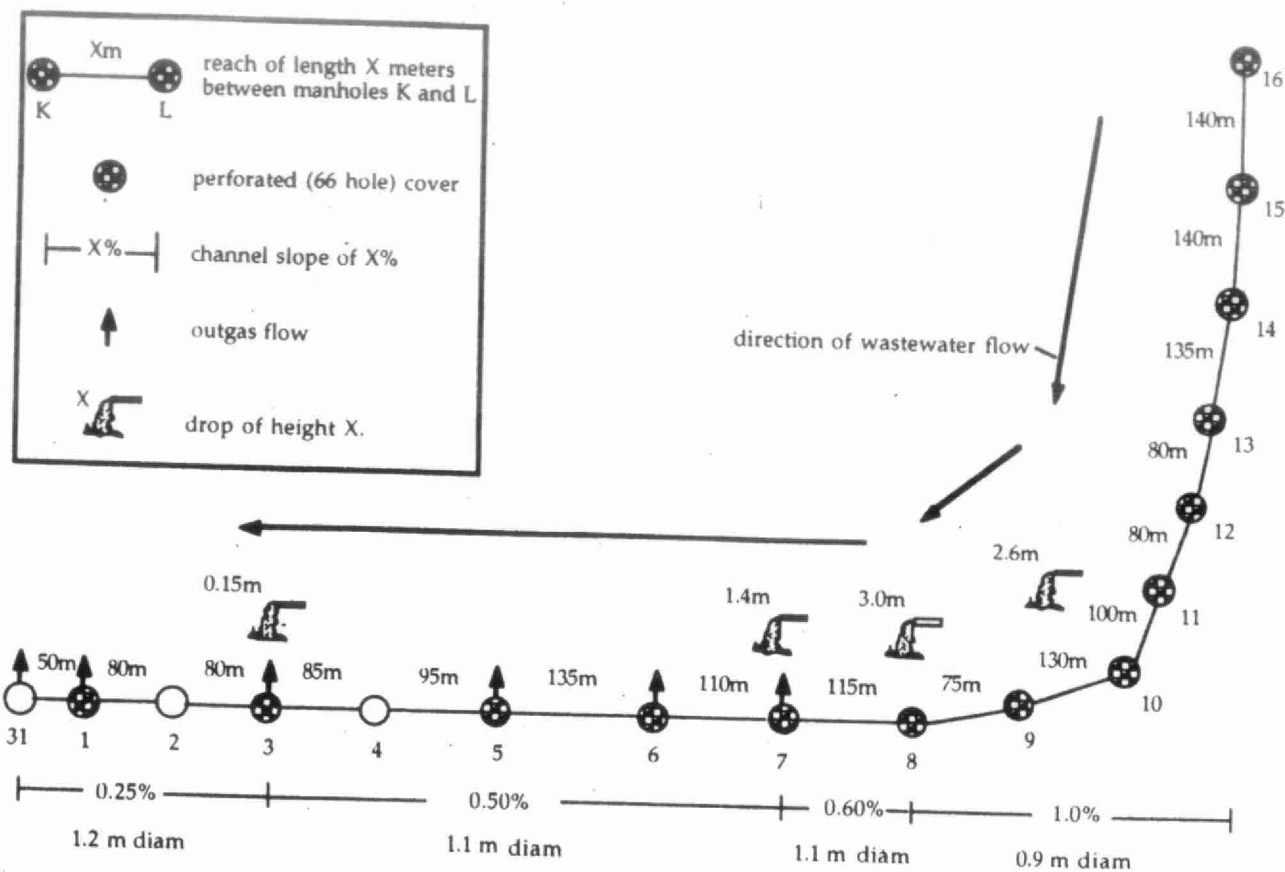


Figure 2. Illustration of the operating sewer used for field experiments.

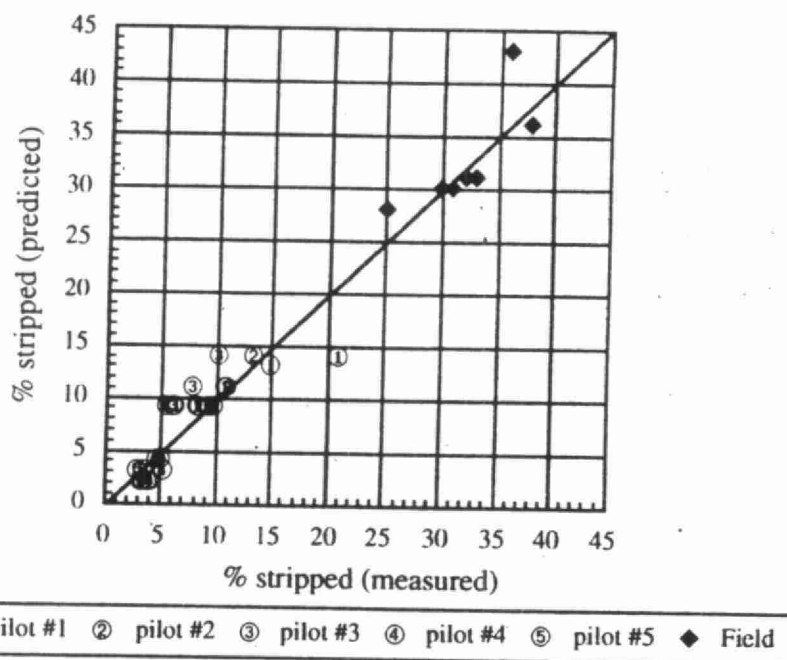


Figure 3. Predicted versus measured VOC stripping efficiencies for pilot and field experiments.

# **Fate of Volatile Organic Compounds in Wastewater Collection Systems**

## **Volume VI: Formation of Chloroform - Pre-Discharge**

Conference Papers

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

September, 1994

94-TA25A.02

# **Residential Washing Machines as Sources of Indoor Air Pollution? Chloroform Formation, Mass Transfer, and Emission Dynamics**

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## INTRODUCTION

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Recent concerns regarding air quality and related human health effects have led to investigations of sources of volatile organic compounds (VOCs) in a wide range of indoor environments. For example, Chan *et al.*<sup>1</sup> completed a study to assess levels of several VOCs, including chloroform, in 12 Ontario homes. Although specific sources were not determined, average chloroform concentrations in living room air were as high as 5 ppb. Chloroform levels in homes are often two or more orders of magnitude higher than in outdoor air.<sup>1-2</sup>

Although it is clear from previous studies that significant indoor sources of chloroform must exist, those sources have not been rigorously studied. However, because chloroform is ubiquitous to chlorinated drinking water, it is reasonable to assume that it is released from locations where potable water comes in contact with indoor air, e.g. sinks, showers, washing machines. Such sources have received some attention for compounds ranging from ethanol to radon.<sup>3-6</sup> Showers have received the most attention.<sup>7-8</sup>

Although there is considerable evidence of rapid chloroform formation following the addition of hypochlorous acid to water<sup>9-10</sup>, there is little published information related to in-home formation and subsequent emissions of chloroform following the use of commercial laundry bleaches. However, conditions inside of a washing machine should often be conducive to chloroform formation. The presence of organic precursors from clothes, free residual chlorine from commercial bleach, elevated wash water temperature and low ammonia concentration promote chloroform formation. Once chloroform is formed, transfer from wash water to air is enhanced by intentional agitation of the wash water, i.e. mixing during wash cycles. Chloroform can then be released to indoor air via several mechanisms, including 1) ventilation of the washing machine headspace during its operation, 2) rapid evacuation/turnover of the washing machine headspace following lid opening, and 3) stripping from wash water during discharge to drain wash basins.

This paper includes a description of experiments completed to determine the extent to which chloroform is generated and subsequently emitted from residential washing machines. Experiments were completed to study the potential for 1) chloroform formation in laundry wash water, 2) gas-liquid mass transfer between wash water and an overlying headspace, and 3) washing machine headspace ventilation and subsequent chloroform emissions to indoor air. A dynamic model was developed to predict transient chloroform emissions during domestic laundry activities. Results presented in this paper should be useful for assessing the relative importance of washing machines as sources of gaseous chloroform emissions to indoor air.

## MODEL DEVELOPMENT

In order to develop a model to predict chloroform emissions, it was necessary to include relationships to predict chloroform formation, gas-liquid mass transfer and release from a washing machine headspace. Relationships were based on the assumption that wash water can be characterized as a well-mixed batch reactor, and the overlying headspace approaches a continuous-flow stirred tank reactor (CFSTR).

Free residual chlorine ( $\text{HOCl}$ ,  $\text{OCl}^-$ ,  $\text{Cl}_2$ ) consumption in the washing machine was assumed to be first order, i.e. dependent only upon the concentration of chlorine remaining in solution, so that:

$$\frac{dX}{dt} = -kX \quad (1)$$

where  
 $X$  = free residual chlorine concentration in  $\text{mg/m}^3$

$k$  = first-order chlorine consumption rate constant in  $\text{min}^{-1}$   
 $t$  = time in min.

Integration of Equation 1 with respect to time leads to:

$$X = X_0 e^{-kt} \quad (2)$$

where

$X_0$  = initial concentration of free residual chlorine in  $\text{mg}/\text{m}^3$ .

Chloroform formation was also modeled as a first-order reaction dependent only upon free residual chlorine concentration in wash water:

$$\frac{dC}{dt} = K'X = K'X_0 e^{-kt} \quad (3)$$

where

$C$  = chloroform concentration in wash water in  $\text{mg}/\text{m}^3$

$K'$  = chloroform formation rate constant in  $\text{min}^{-1}$

$V_1$  = wash water volume in  $\text{m}^3$ .

In order to model mass transfer of chloroform from wash water to an overlying headspace, the following mass balance equation for a well-mixed batch reactor applies:

$$V_1 \frac{dC}{dt} = -K_L \left( C - \frac{C_g}{H_c} \right) A + K'X_0 e^{-kt} V_1 \quad (4)$$

where

$C_g$  = chloroform concentration in the headspace in  $\text{mg}/\text{m}^3$

$A$  = gas-liquid surface area in  $\text{m}^2$

$K_L$  = overall gas-liquid mass transfer coefficient in  $\text{m}/\text{min}$

$H_c$  = Henry's law coefficient in  $\text{m}^3_{\text{liq}} / \text{m}^3_{\text{gas}}$ .

A corresponding expression was developed by performing a mass balance on the reactor headspace:

$$V_g \frac{dC_g}{dt} = Q_g C_{gi} - Q_g C_g + K_L \left( C - \frac{C_g}{H_c} \right) A \quad (5)$$

where

$C_{gi}$  = chloroform concentration in gas entering the machine headspace in  $\text{mg}/\text{m}^3$

$Q_g$  = headspace ventilation rate in  $\text{m}^3/\text{min}$

$V_g$  = washing machine headspace volume in  $\text{m}^3$ .

Equations 4 and 5 form a system of linear, non-homogeneous, ordinary differential equations that can be solved analytically or numerically to estimate liquid and gas-phase chloroform concentrations, and subsequent emission rates ( $= Q_g C_g$ ) as functions of time.

### Chloroform Formation Experiments

Chloroform formation experiments were performed in a standard residential washing machine (Kenmore Series 29901), with the objective of determining values of  $k$  and  $K'$  in Equations 2 and 3, respectively. Three variations of the experiment were performed, including 1) with clothes in the machine, 2) with clothes removed from the machine after a 10 minute pre-wash cycle, and 3) without clothes having been added to the machine. Clothes were always obtained from the same adult source, and represented a mix of white undergarments and shirts. Experiments were completed using City of Guelph chlorinated groundwater. Background chloroform concentrations in the water supply were typically less than 5 µg/L.

Experiments with clothes required filling the washing machine with warm water, adding 75 mL of a commercially-available detergent (Ultra Tide Free®) and 250 mL of bleach (Javex®, 5.7% as  $\text{Cl}_2$ ). Wash water volume was recorded for each experiment and temperature was measured using a standard mercury thermometer. Wash water mixing was allowed to occur for approximately one minute prior to sample collection. Initial free residual chlorine and chloroform samples were collected prior to clothes being added. Mixing was then allowed to continue for approximately 10 seconds prior to collection of a liquid sample for subsequent initial total organic carbon (TOC), total suspended solids (TSS), volatile suspended solids (VSS) and pH determination. Free residual chlorine and chloroform sampling continued at regular intervals over a thirty minute period. A sample was collected at the end of the thirty minute period for determination of final TOC concentration. Samples to be used for chloroform analysis were all collected in 20 mL crimp-top glass vials with teflon-lined septum. Each vial contained 0.5 g of sodium sulfite to scavenge residual chlorine and quench chloroform formation following sample collection. Separate glass beakers were used to complete N,N-diethyl-p-phenylenediamine (DPD) titrations to determine free residual chlorine concentration as a function of time after bleach addition.

The second type of experiment involved the completion of a regular 10 minute wash cycle with clothes, warm water and detergent. After completion of the cycle, the clothes were removed and excess water was wrung back into the washing machine. Water volume was recorded and an initial sample was collected for TOC and solids analysis. Commercial bleach was added to the water and a standard wash cycle was initiated. A sampling procedure was then followed as described above.

Finally, a third type of experiment was performed in which no clothes were added to the washing machine. The machine tub was filled with warm water as before and detergent and bleach were added. Free residual chlorine, chloroform, TSS and TOC samples were collected over a thirty minute period as described above.

For each experiment, first-order reaction rate constants for chlorine were determined as the slope of a linear best-fit of  $\ln(X/X_0)$  versus time in accordance with Equation 2. Chloroform formation rate constants were similarly determined by integration of Equation 3 and subsequent plots of  $(C - C_0)/X_0$  versus  $(1 - e^{-kt})$ . This approach required an assumption that only a small fraction of the total chloroform generated in the wash water was transferred to the machine headspace, a condition which has been reported elsewhere.<sup>11</sup> For all experiments, values of  $R^2$  associated with best-fit equations ranged from 0.93 to 0.999.

### Chloroform Mass Transfer Experiments

Mass transfer experiments were performed in the washing machine described previously, with the objective of determining system-specific mass transfer coefficients as described below. Modifications made to the machine are illustrated in Figure 1. A plexiglass lid was constructed to facilitate headspace ventilation and liquid sampling. Two 10 cm holes were cut into the lid to serve as inlet and outlet vents, while a 2.5 cm hole was used for sampling. A short section of 10 cm dryer hose was attached to the inlet vent, extending to a commercial blower which served as a source of ventilation. An elbow was placed just

inside the inlet port to prevent impingement of air directly onto the water surface. The interior of the machine was completely sealed to ensure that total air flow exited through the exhaust stack, which was directly connected to a fumehood. Ventilation rate measurements were made using a hot-wire anemometer inserted into a small, sealable hole on the side of the exit stack. Two 0.6 cm holes were drilled into a cork stopper which was then inserted into the sampling hole. A thermocouple and a section of teflon® tubing were passed through these holes and into the wash water. A peristaltic pump was used to continuously draw liquid samples from wash water at a rate of 30 mL/min during experiments.

Three types of mass transfer experiments were performed: 1) with no clothes added, 2) with 2.3 kg of clothes added, and 3) with 4.5 kg of clothes added. Each of these experiments was performed twice. Two additional experiments were completed without detergent (0 and 4.5 kg of clothes). For all experiments, wash water volume was set to high (74 L) and temperature was set to warm (approximately 30 °C). Headspace ventilation was consistently greater than 200 turnovers per hour, thus preventing gas-phase accumulation of chloroform.

At the start of each experiment, the washing machine was filled and temperature and volume measurements were recorded. A glass vial containing 50 mL of chloroform dissolved in methanol was added to the wash water to yield an initial concentration of approximately 1.0 mg/L. The water was allowed to mix for a short time before clothes and/or detergent were added. Over a 60 minute period, liquid samples were then collected with zero headspace in 20 mL glass vials with teflon®-lined septa.

Data from mass transfer experiments were plotted according to the following expression, which results from integration of a mass balance on the wash water:

$$\ln\left(\frac{C}{C_0}\right) = -K_{L,a} t \quad (6)$$

where

$$a = A/V_1 \text{ in } 1/\text{m}.$$

The slope of a linear best-fit of the curve obtained by plotting  $-\ln(C/C_0)$  versus time was used to determine system-specific mass transfer coefficients,  $K_{L,a}$ . Values of  $R^2$  exceeded 0.95 for all mass transfer experiments.

#### Headspace Ventilation Experiments

In order to investigate natural ventilation of a domestic washing machine, tracer experiments were carried out using sulfur hexafluoride ( $\text{SF}_6$ ). It was assumed that the headspace was well-mixed and behaved as a CFSTR. Three liquid volume settings were tested: medium (61 L), high (74 L) and extra high (90 L). At the start of each experiment, a known quantity of pure  $\text{SF}_6$  was injected into the headspace of the machine through a 0.6 cm sample port. A 30 cm segment of 0.6 cm i.d. teflon® tubing was inserted into the port, allowing tracer injection and sampling to occur close to the center of the headspace volume. Following tracer injection, samples were collected in 10 mL stop-cock syringes at 30 second intervals for a period of four minutes. The sample port was flushed immediately prior to filling each sample syringe in order to ensure that stagnant air did not accumulate in the sample line. Sulfur hexafluoride data were analyzed according to:

$$\ln\left(\frac{S}{S_0}\right) = -\frac{1}{\theta} t \quad (7)$$

where

$$S = \text{SF}_6 \text{ concentration in the machine headspace in mg/m}^3 \text{ at time } t \text{ in min}$$

$S_0$  = initial  $\text{SF}_6$  concentration in the machine headspace in  $\text{mg/m}^3$   
 $\theta$  = average residence time for a compound in a machine headspace in min.

A linear, best-fit regression equation for the resulting curve produced the inverse value of headspace residence time ( $\theta$ ). Headspace volume was then divided by  $\theta$  to obtain the ventilation rate ( $Q_g$ ). Values of  $R^2$  exceeded 0.95 for all ventilation experiments.

#### Analytical Methods

Chloroform analyses were performed using a gas chromatograph (Hewlett Packard, 5890 Series II) with an electron capture detector (GC/ECD). Sample introduction was performed through the use of a headspace concentrator with a multi-vial carousel (Hewlett Packard, 19395A). Vials were maintained at  $30^\circ\text{C}$  in a temperature-regulated oil bath for four hours prior to analysis. For each sample, the initial GC oven temperature was  $31^\circ\text{C}$ , held for 1 minute and ramped at  $10^\circ\text{C/min}$  to  $100^\circ\text{C}$ , where it was held for 4 minutes. A J&W Scientific, 30 m DB-5 (0.32 mm i.d. with  $1.0\ \mu\text{m}$  film thickness) capillary column was used for all analyses.

Sulfur hexafluoride analyses were carried out by manual injection into the previously described GC/ECD. Oven temperature was held at  $31^\circ\text{C}$  for the duration of each 2 minute run. All other analyses (TSS, VSS, TOC, pH,  $\text{Cl}_2$ ) were completed according to Standard Methods.<sup>12</sup>

## RESULTS AND DISCUSSION

Several parameters were measured during residual chlorine reaction and chloroform formation experiments. For seven of eight experiments, pH following bleach addition ranged from 8.4 to 8.8. The pH for Experiment 5 was 9.0. Initial free residual chlorine concentrations ranged from 280 to  $380\ \text{mg/L}$ , and were greatest when clothes were removed from the machine prior to bleach addition, i.e. due to the lower wash water volume. Wash water volumes ranged from 38 to 50 L. Values of wash water temperature, clothes loading, TSS, VSS, and TOC are listed in Table 1 for each experiment. The type of experiment (clothes, clothes removed, and no clothes) is also indicated. Measureable quantities of TSS, VSS, and TOC were observed for experiments that did not include clothes addition, likely resulting from laundry detergent. Analysis of TOC was not completed for the first two experiments. For remaining experiments that involved a pre-wash (Experiments 4 and 7), TOC concentrations did not change appreciably over the course of each 30 minute experiment. In each case, TOC was observed to decrease by 3%, possibly due to liquid-to-gas transfer of the volatile portion of TOC. For Experiment 6, TOC concentration increased from 376 to  $492\ \text{mg/L}$  over 30 minutes, presumably as a result of continuous surfactant removal of organics from the surface of clothes.

#### Residual Chlorine Removal

During each experiment, ten separate samples were collected and analyzed to determine temporal reduction in free residual chlorine. Subsequent values of  $k$  for each experiment are listed in Table 1. As expected, maximum values of  $k$  occurred in the presence of clothes and ranged from  $0.068$  to  $0.15\ \text{min}^{-1}$ . Values of  $k$  for experiments with clothes removed ranged from  $0.016$  to  $0.034\ \text{min}^{-1}$ . Finally, values of  $k$  were negligible when clothes were never added to the wash water. These results clearly suggest that a significant amount of chlorine is reacted on the surface of clothes, but that some may also react with other compounds dissolved or suspended in wash water. Very little chlorine reacts with compounds present in clean potable water, or with detergent added to such water.

#### Chloroform Formation

A major objective of this study was to determine the extent of chloroform formation during a wash cycle in a typical domestic washing machine. Chloroform concentrations at the end of a ten minute wash cycle ( $\text{C}_{10}$ ) are listed in Table 1, and ranged from  $50\ \mu\text{g/L}$  when no clothes were added to the wash, to  $1500$

$\mu\text{g/L}$  (Experiments 3 and 4). This leads to chloroform yield coefficients ( $\mu\text{g}$  of chloroform per mg of  $\text{Cl}_2$ ) ranging from 0.16 to 5.2  $\mu\text{g/mg}$ . For those experiments which included clothes throughout the wash cycle, the yield coefficient ranged from 2.7 to 5.2  $\mu\text{g/mg}$ , with an average of 4.2  $\mu\text{g/mg}$ . These values are consistent with a range of 0.6 to 8  $\mu\text{g/mg}$  reported previously for chlorination of swimming pools.<sup>13</sup>

Chloroform formation data are presented graphically in Figures 2-4, while formation rate constants ( $K'$ ) are listed in Table 1. Similar amounts of chloroform were formed during experiments involving clothes and clothes removal. This was particularly true during the first ten minutes of each experiment, even though the concentration of free residual chlorine in wash water was significantly depleted during experiments involving clothes. One possible explanation for this observation is that chloroform may actually be formed via surface reactions involving chlorine and organic precursors, as well as by reactions in wash water.

### Gas-Liquid Mass Transfer

A total of eight mass transfer experiments were performed. Data were plotted in accordance with Equation 6 to determine values of  $K_L a$ . Corresponding plots are shown in Figures 5-7. Values of  $K_L a$  are presented in Table 2.

The highest  $K_L a$  value was observed for the experiment where neither detergent nor clothes were added to the wash cycle (Experiment 9). Addition of clothes resulted in a decrease in mass transfer coefficient by approximately 70%. There was effectively no difference between mass transfer coefficients when 2.3 kg and 4.5 kg of clothes were added. A significant increase in  $K_L a$  occurred during experiments without clothes addition (Experiments 11 and 14). The presence of clothes in wash water tends to dampen kinetic energy associated with agitation of the wash water, with a subsequent reduction in splashing at the wash water surface. A marked increase in surface agitation was observed when experiments were completed without clothes addition.

Mass transfer coefficients were also affected by the addition of detergent. Both experiments where detergent was used without clothes addition had mass transfer coefficients of approximately  $0.03 \text{ min}^{-1}$ , factors of  $2^+$  lower than  $K_L a$  for Experiment 9. Relative to Experiment 10 (no detergent), slightly lower  $K_L a$  values were observed for those experiments involving detergent and 4.5 kg of clothes.

### Headspace Ventilation

Six ventilation experiments were completed, in which three different washing machine water volume settings were tested. Results are presented in Table 3. Washing machine ventilation rate ( $Q_g$ ) decreased with increasing liquid volume. However, the headspace turnover rate of the machine was relatively constant for all experiments, with an average value of 1.3 air exchanges per minute. This high value implies that washing machines are so well-ventilated that appreciable chloroform accumulation in the headspace is unlikely, i.e. the system should remain far from equilibrium as defined by Henry's law.

### Model Applications and Analyses

McKone<sup>4</sup> reported radon stripping efficiencies of 90% for laundry activities, and suggested a multiplier of 0.75 for chloroform, i.e. chloroform stripping efficiency of 68%. Wooley *et al.*<sup>6</sup> quantified ethanol emissions from household washing machines. Typical laundry (LT) and high release laundry (LH) conditions were defined based on wash and rinse water temperatures. For three experiments, the average ethanol stripping efficiencies were reported to be 0.2% for LT and 1.1% for LH. Although these stripping efficiencies are low, it is inappropriate to assume that stripping efficiencies for chloroform are similarly low. At 25 °C, the Henry's law coefficient for chloroform is approximately three orders of magnitude greater than ethanol. In the case of ethanol, gas-phase resistance to mass transfer is likely to dominate overall mass transfer from wash water to a washing machine headspace. Furthermore, the headspace may become effectively saturated (approach equilibrium) with ethanol during a wash cycle, thus significantly retarding mass transfer.



For this study, Equation 6 was solved using experimental values of  $K_L a$  to determine chloroform stripping efficiencies over a 10 minute wash cycle, i.e. assuming that chloroform enters the machine in potable drinking water and is not formed during washing. It was assumed that the machine headspace was sufficiently well-ventilated that gas accumulation could be ignored. The validity of such an assumption is discussed later in this section. Resulting stripping efficiencies ranged from 10 to 18%, with an average of 15% over eight mass transfer experiments. As expected, these values are significantly higher than those reported previously for ethanol.<sup>6</sup> However, they are much lower than those reported by McKone.<sup>4</sup>

A chloroform concentration of 50 mg/m<sup>3</sup> is reasonable for chlorinated drinking water originating from surface water sources, and will be used for comparative purposes in the remainder of this section. Such a concentration coupled with 15% stripping from 61 L of wash water (Experiments 17 and 18; medium volume setting) would result in approximately 0.5 mg of chloroform released from a washing machine without bleach addition. The actual value would likely be higher, as chloroform emissions during spray-filling of the machine were not accounted for in the above approximation.

Mass emissions of chloroform were also estimated for "typical" washing machine conditions in which chlorinated bleach is used. Equations 4 and 5 were solved simultaneously using a finite difference time-stepping algorithm. Parameters used in the analysis are listed in Table 4. An initial liquid concentration of 50 mg/m<sup>3</sup> was again assumed. The value of  $K_L a = 0.016/\text{min}$  was an average of those mass transfer experiments in which clothes were submerged in wash water. Values of  $k$ ,  $K'$  and  $X_0$  were consistent with Experiment 3. Values of liquid and gas volumes were consistent with Experiments 17 and 18 (medium setting). Headspace ventilation rate ( $Q_g$ ) was taken to be the average value obtained from Experiments 17 and 18. A value of  $H_c = 0.23 \text{ m}^3 \text{ liq} / \text{m}^3 \text{ gas}$  at 34 °C was estimated based on the work of Ashworth *et al.*<sup>14</sup>

Based on the aforementioned parameters, it was estimated that a 10 minute wash cycle with bleach addition leads to approximately 7 mg of chloroform released to indoor air. This value would be greater if stripping of initial chloroform was accounted for during machine filling. In the worst-case, all of the chloroform released during filling would have increased emissions by 3 mg. Furthermore, based on headspace volume and final gas-phase chloroform concentration (12 mg/m<sup>3</sup>), an additional 1 mg of chloroform would have been released during lid opening. Thus, a total release of 11 mg of chloroform was possible for the laundry event. A range of 8 to 11 mg is assumed for the remainder of this analysis.

It was desired to compare emissions of chloroform from washing machines with those from showers. Based on the work of Giardino *et al.*<sup>7</sup> and McKone and Knezovich<sup>8</sup>, a chloroform stripping efficiency of 50% from showers was assumed to be reasonable. Thus, a liquid chloroform inlet concentration of 50 mg/m<sup>3</sup> with an assumed volume of 40 L/shower leads to approximately 1 mg of chloroform release. These results suggest that chloroform emissions from a single load of non-chlorinated laundry may be approximately the same as from a single showering activity. Furthermore, emissions from a single load of chlorinated laundry may be approximately an order of magnitude greater than emissions from showers, even though the latter have received significantly greater attention in the published literature.

The results described above address only a unit activity and do not account for human exposure, i.e. direct human inhalation exposure occurs during showering but may not occur during laundry activities. Furthermore, total chloroform releases for each activity on a per capita basis should account for the frequency of activities.

For the purposes of this approximation, it was assumed that each individual showers once per day, leading to total chloroform emissions from showers of 365 mg/person\*year. To estimate chloroform emissions from laundry activities, a laundry water usage estimate of 16 L/person\*day was employed.<sup>15</sup> At 61 L per wash, this value suggests an average of 96 wash cycles/person\*year. This leads to an estimate of 48

mg/person•year from laundry activities that do not involve the use of chlorinated bleach. Rogozen *et al.*<sup>10</sup> provided U.S. market-based data which indicated an approximate chlorine usage of 0.23 kg/person•year for domestic laundry activity. This value may be conservative based on bleach usage patterns, but was used as a rough approximation here. Based on recommended quantities of bleach addition, it was estimated that the average number of bleached laundry loads/person•year is 13. This value leads to estimated total chloroform releases of 104 to 141 mg/person•year. The total of bleached and non-bleached chloroform releases is thus estimated to range from approximately 150 to 190 mg/person•year, somewhat lower than, but on the same order of magnitude as, those for showering.

The ratio of predicted gas-to-liquid chloroform concentrations was evaluated to determine the degree to which gas accumulation in a washing machine headspace approached equilibrium, i.e. as defined by Henry's law. The degree of equilibrium increased throughout the 10 minute wash cycle, but was only 4.3% at the conclusion of the cycle. Thus, the two-phase model results presented here suggest that it may be valid to assume that a washing machine headspace is infinitely ventilated, i.e. effectively open to room air, during a 10 minute wash cycle.

Finally, the authors acknowledge that while many experiments were completed for purposes of parameter estimation, the model described in this paper has not been rigorously evaluated using independent experiments. Such experiments will be completed during the next phase of research.

## SUMMARY AND CONCLUSIONS

This paper provides a description of a screening study completed to determine the potential for chloroform emissions from household washing machines. The following observations and conclusions were made:

1. Laundry wash water contains surrogates necessary for the formation of chloroform.
2. Chlorine reacts quickly in washing machines, in part to form chloroform.
3. Significant levels of chloroform can be generated following the addition of bleach to wash water.
4. During wash cycles, the gas-liquid mass transfer process associated with chloroform transfer from wash water to headspace does not approach equilibrium.
5. Chloroform stripping efficiencies from washing machines far exceed those previously reported for the less-volatile compound ethanol. However, for this study the average chloroform stripping efficiency of 15% was significantly lower than those reported previously based on radon transfer.
6. On a unit activity basis, chloroform emissions from washing machines into which chlorinated bleach has been added far exceed chloroform emissions from a showering activity.
7. On an annual basis, chloroform emissions from washing machines are likely to be of the same order of magnitude, but slightly less than, chloroform emissions from showers.

Based on the results of this study, it appears that laundry activities can be major contributors to chloroform concentrations in households that use bleach containing sodium hypochlorite. However, these results are not sufficient in scope to determine the need for concerns related to such emissions. The results do indicate that while showers have received significant attention as sources of volatile indoor air contaminants, other sources involving gas-liquid mass transfer may warrant similar attention.

## ACKNOWLEDGEMENTS

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Table 1. Experimental conditions and results for chloroform formation experiments.

Expt #	Expt type	Temp (°C)	Clothes (kg)	TSS/VSS (mg/L)	TOC initial/final (mg/L)	CHCl <sub>3</sub> (@ 10 min) (µg/L)	k (min <sup>-1</sup> )	K' (min <sup>-1</sup> )
1	C	32	2.3	166/52	NA/NA	1400	0.068	0.00068
2	CR	32	2.3	203/51	NA/NA	1000	0.016	0.00021
3	C	34	3.2	274/109	292/NA	1500	0.124	0.00085
4	CR	35	3.2	237/81	381/370	1500	0.034	0.00033
5	NC	35	0.0	215/49	205/NA	100	0.001	0.000015
6	C	36	3.6	393/178	376/492	800	0.151	0.00062
7	CR	36	3.6	318/185	378/366	650	0.028	0.00012
8	NC	36	0.0	180/35	148/NA	50	0.000	0.000013

NA = not available; C = clothes in machine throughout experiment; CR = clothes removed from machine after one pre-wash cycle and before bleach addition; NC = no clothes added to machine.

Table 2. Experimental conditions and results for mass transfer experiments.

Expt #	Clothes (kg)	Temperature (°C)	$K_L a$ ( $\text{min}^{-1}$ )
9 <sup>a</sup>	0	31	0.07
10 <sup>a</sup>	4.5	31	0.02
11	0	32	0.028
12	2.3	31	0.013
13	4.5	29	0.010
14	0	33	0.029
15	2.3	31	0.020
16	4.5	30	0.019

a: no detergent was added during Experiments 9 and 10.

Table 3. Experimental conditions and results for ventilation experiments.

Expt #	Volume (L)		Ventilation	
	liquid	headspace	(L/min)	(TPM) <sup>a</sup>
17	61	68	82	1.21
18	61	68	98	1.44
19	74	55	83	1.45
20	74	55	72	1.26
21	90	39	51	1.31
22	90	39	48	1.23

a: TPM = headspace volumetric turnovers per minute.

Table 4. Parameters and initial conditions used to model chloroform emissions.

$C_0$	=	50 mg/m <sup>3</sup>	initial liquid-phase concentration of chloroform
$C_{g0}$	=	0 mg/m <sup>3</sup>	initial gas-phase concentration of chloroform
$K_L a$	=	0.016 min <sup>-1</sup>	(see note a)
$k$	=	0.12 min <sup>-1</sup>	
$K'$	=	$8.5 \times 10^{-4}$ min <sup>-1</sup>	
$X_0$	=	290,000 mg/m <sup>3</sup>	
$V_l$	=	0.061 m <sup>3</sup>	
$V_g$	=	0.068 m <sup>3</sup>	
$Q_g$	=	0.090 m <sup>3</sup> /min	
$H_c$	=	0.23 m <sup>3</sup> liq / m <sup>3</sup> gas	

(a). Note that both the left and right-hand-sides of Equations 4 and 5 can be divided by  $V_l$  to yield  $K_L a$  ( $= K_L A/V_l$ )

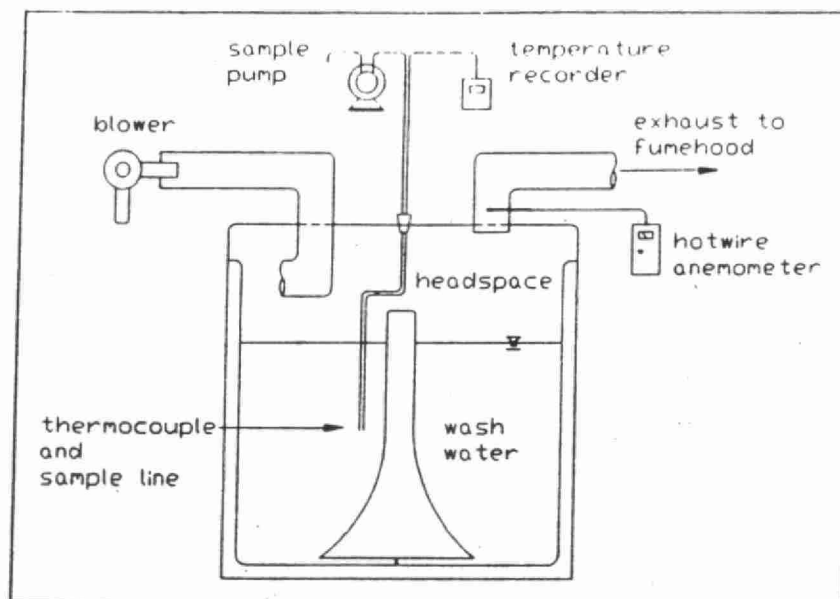


Figure 1. Experimental arrangement used for mass transfer experiments.

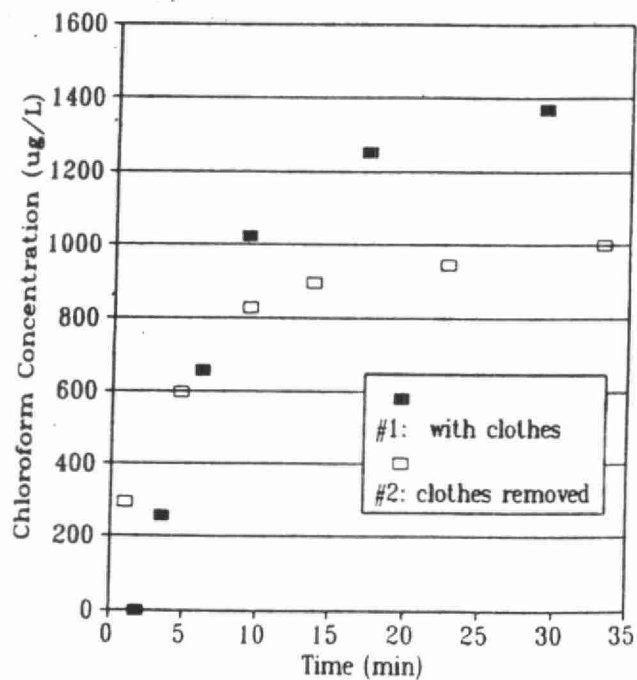


Figure 2. Chloroform formation in wash water versus time after bleach addition (Experiments 1 and 2).

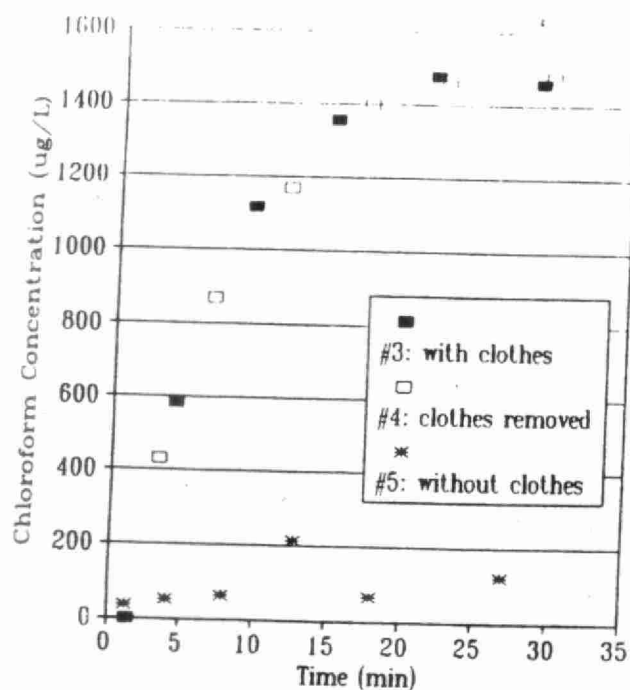


Figure 3. Chloroform formation in wash water versus time after bleach addition (Experiments 3-5).

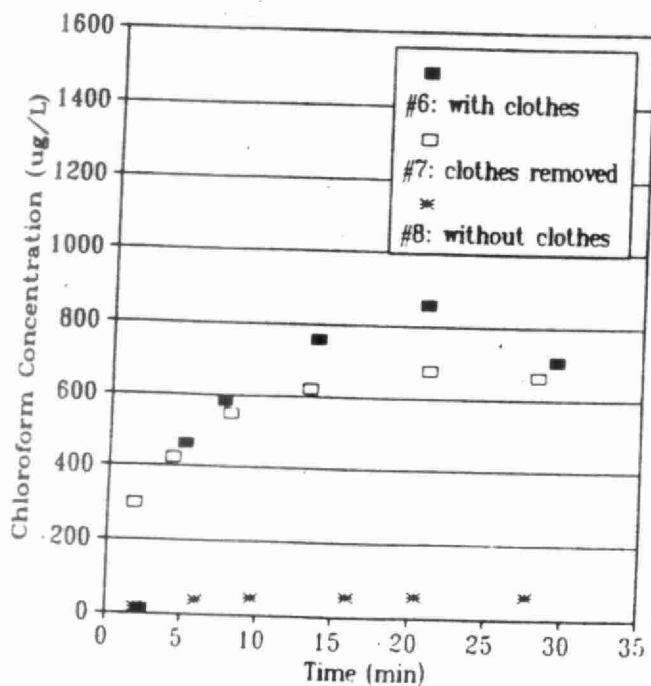


Figure 4. Chloroform formation in wash water versus time after bleach addition (Experiments 6-8).

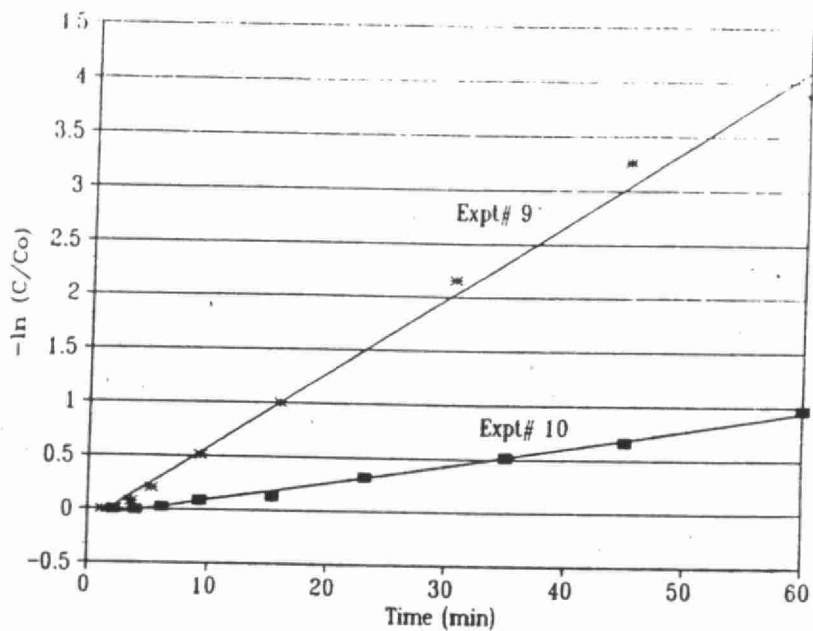


Figure 5. Chloroform release from wash water as a function of time (Experiments 9 and 10).

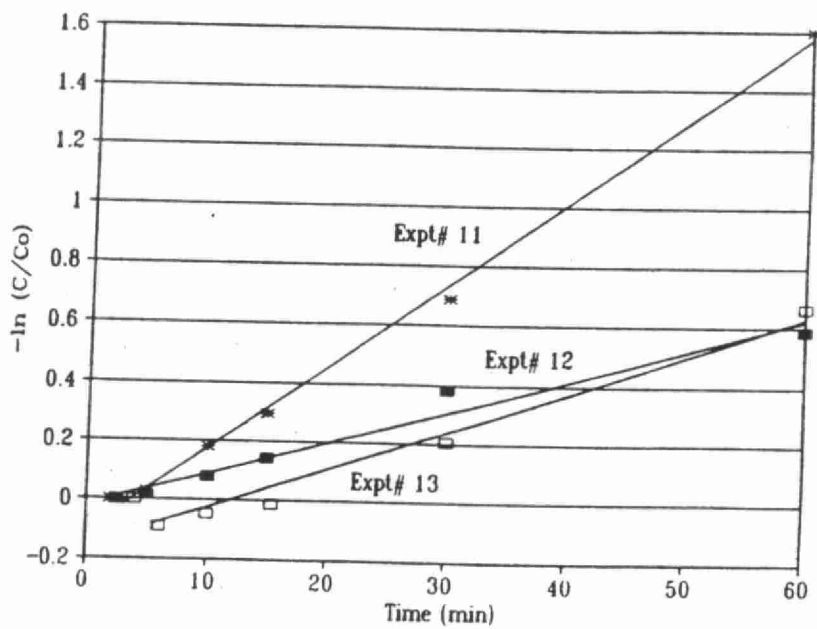


Figure 6. Chloroform release from wash water as a function of time (Experiments 11-13).

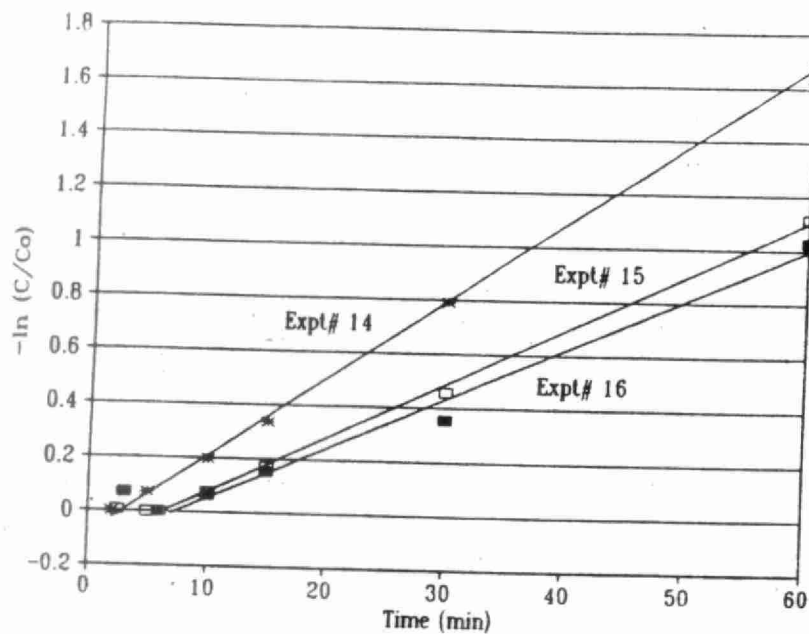


Figure 7. Chloroform release from wash water as a function of time (Experiments 14-16).

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## Generation of Chloroform in Homes

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## INTRODUCTION

Trichloromethane (chloroform) is classified by the United States Environmental Protection Agency as a probable human carcinogen based on sufficient animal evidence.<sup>1</sup> In particular, it is believed to be a hepatocarcinogen with potency factors of  $6.1 \times 10^{-3}$  (mg/kg/day)<sup>-1</sup> and  $8.1 \times 10^{-2}$  (mg/kg/day)<sup>-1</sup>, for ingestion and inhalation exposures, respectively.<sup>2</sup> Chloroform is a volatile organic compound (VOC) with an affinity for the gas phase. Following emissions to the atmosphere, it degrades slowly due mostly to reactions with hydroxyl radicals.<sup>3</sup> Gaseous concentrations of chloroform in the ambient atmosphere range from approximately 16 parts per trillion by volume (ppt) in clean arctic air to as high as 5,000 to 10,000 ppt (5 to 10 parts per billion by volume (ppb)) with reported averages of 820 ppt in industrialized urban centers in the United States<sup>3</sup>, and 630 ppt across over 3600 data points associated with a range of outdoor site types in the United States.<sup>4</sup>

Concentrations of chloroform in homes are often two or more orders of magnitude higher than in outdoor air.<sup>4-5</sup> Thus, substantial indoor sources of chloroform must exist. Previous studies of chloroform in indoor air have focused on emissions due to the use of chlorinated drinking water, e.g. in showers.<sup>6</sup> Although there is ample evidence of chloroform formation following the addition of hypochlorous acid to water,<sup>7-11</sup> there is a paucity of published information related to in-home formation and subsequent emissions of chloroform following the use of commercial laundry bleaches containing sodium hypochlorite.

This paper provides a summary of initial experiments completed to assess the potential and approximate magnitude of chloroform formation in laundry wash water and accumulation in the headspace of washing machines. The intent was not to determine the complex chemical reaction mechanisms associated with chloroform formation, relative risks associated with laundry activities, or mass transfer dynamics between wash water and laundry room air, although the latter will be the focus of future (phase II) studies. Instead, preliminary studies were intended to serve as a "screening" phase to determine the extent to which chloroform forms in washing machines and whether further studies of washing machines as indoor sources of chloroform are warranted.

## BACKGROUND

Several researchers have reported the generation of trihalomethanes (THMs), principally chloroform, and other volatile and non-volatile halogenated organic compounds following the addition of hypochlorous acid to water and wastewater.<sup>7-11,12</sup> Although not completed using laundry wash water, the results of previous studies suggest that if the appropriate organic precursors are present in wash water, the amounts of sodium hypochlorite routinely added to household washing machines should form significant quantities of chloroform. Once chloroform is formed, its transfer from wash water to air should be enhanced by elevated wash water temperatures and significant agitation/mixing of the wash water. Following its formation, chloroform can be released to indoor air via three primary mechanisms:

1. diffusion or buoyant air transport out of the enclosed washing machine headspace,
2. rapid evacuation/turnover of the washing machine headspace following lid opening, and
3. stripping from wash water during its drainage at the end of a wash cycle, particularly associated with discharges to tubs/sinks adjacent to washing machines.

The remainder of this section provides a description of levels and sources of chloroform in residential indoor air.

### Levels and Sources of Chloroform in Indoor Air

A recent study was completed to assess levels of several VOCs, including chloroform, in 12 Ontario homes.<sup>5</sup> Although specific sources were not determined, average chloroform concentrations in living room air were as high as  $25 \mu\text{g}/\text{m}^3$ , and up to 125 times higher than concentrations observed in ambient air. Shah and Singh<sup>4</sup> presented data which confirm elevated levels of chloroform in indoor environments. They reported average and median daily concentrations, based on 2120 sample points, in U.S. indoor environments of 0.83 and 0.10 ppb, respectively. It is clear from previous studies that significant indoor sources of chloroform must exist.

Sources of chloroform emissions to indoor air have not been rigorously studied. However, because chloroform is ubiquitous to chlorinated drinking water, it is reasonable to assume that it is released from locations where potable water comes in contact with indoor air (e.g., sinks, dishwashers, bath tubs, showers, water used for cooking, and washing machines). All of these sources have received some attention in the published literature for compounds ranging from radon to trichloroethene.<sup>6,13-18</sup> Showers have received the most attention.<sup>19-20</sup>

Giardino *et al.*<sup>19</sup> described the use of sulfur hexafluoride ( $\text{SF}_6$ ) as a surrogate for volatilization of organics from indoor water uses, and experimentally observed 36-52% relative stripping of  $\text{SF}_6$  from shower water. Furthermore, it was argued that although chloroform is less volatile than  $\text{SF}_6$ , in terms of equilibrium air-water partitioning coefficients, mass transfer limitations yield similar stripping rates for chloroform and  $\text{SF}_6$ . McKone *et al.*<sup>20</sup> completed experiments to determine the transfer efficiency of TCE from water to air in showers. They observed an arithmetic mean transfer efficiency of 61% over 8 experiments, slightly higher than the transfer efficiencies observed by Giardino *et al.* They concluded that inhalation exposures to TCE in showers are approximately equivalent to those for ingestion contact of 1 to 4 liters of water per day. Carcinogen potency factors for the oral route and inhalation route are similar for TCE;  $1.1 \times 10^{-2}$  and  $1.3 \times 10^{-2} (\text{mg}/\text{kg}/\text{day})^{-1}$ , respectively.<sup>2</sup> The inhalation potency factor is more than an order of magnitude greater than the ingestion potency factor for chloroform. Thus, the results of McKone *et al.*<sup>20</sup> suggest that inhalation of chloroform in indoor air should be of much greater concern than the ingestion of chloroform in drinking water. Furthermore, these results relate only to inhalation during showering, and do not account for in-home generation of chloroform due to the use of sodium hypochlorite in some laundry bleaches.

Wooley *et al.*<sup>18</sup> quantified ethanol emissions from household washing machines. Typical laundry (LT) and high release laundry (LH) conditions were defined based on wash and rinse water temperatures. For three experiments, the average ethanol stripping efficiencies were reported to be 0.2% for LT and 1.1% for LH. Although these stripping efficiencies are low, it is inappropriate to assume that stripping efficiencies for chloroform are similarly low. At  $25^\circ\text{C}$ , the Henry's law constant for chloroform is approximately three orders of magnitude greater than ethanol. In the case of ethanol, gas-phase resistance to mass transfer is likely to dominate overall mass transfer from wash water to a washing machine headspace. Furthermore, the headspace may become effectively saturated (approach equilibrium) with ethanol during a wash cycle, thus significantly retarding mass transfer. Results of this study suggest that the latter does not occur for chloroform.

McKone<sup>6</sup> summarized two research efforts intended to quantify radon transfer efficiencies from household tap water to indoor air. Results are presented in Table I for several water consumption categories. The third column in Table I was added for this study and is simply the product of average radon transfer efficiencies and water consumption. Thus, it reflects relative source strengths of each consumptive use category assuming equal pollutant concentrations in the inlet to each category (a reasonable assumption for pollutants in potable water). If the ratio of chloroform-to-radon transfer efficiencies is the same for each system, it is reasonable to conclude that chloroform emissions from laundry activities and bathing/showering are of comparable magnitude. McKone<sup>6</sup> suggested a ratio of chloroform-to-radon transfer efficiencies of 0.75. However, this ratio must be used with some caution for enclosed systems where accumulation in the gas phase can cause differences in mass transfer for compounds with different equilibrium air-water partition coefficients. Nevertheless, if the aforementioned argument related to the relative magnitudes of chloroform emissions from showers and washing machines is even approximately valid, laundry activities may dominate bathing activities if appreciable chloroform is formed in washing machines.

TABLE I. Water-use categories: relative importance of radon transfer from tap water to air.

Source category	Radon transfer efficiency (%)	Water consumption (L/person/day)	Transfer x Use
Toilets	30	35 - 95	11 - 29
Showers	63 - 65	25 - 75 (combined)	16 - 48 (combined)
Baths	30 - 47		
Laundry	90	28 - 44	25 - 40
Dishwasher	90 - 98	14	13
Kitchen and sinks	30	19 - 68	6 - 20
Cleaning	90	13 - 30	12 - 27

## METHODOLOGY

No standard methodology exists for collection of VOCs in household appliances. This section provides a summary of the methodology used for collecting and analyzing washing machine samples, with an emphasis on washing machine headspace (air) samples for preliminary experiments. Methodologies are continuing to be developed for the next phase of experimentation.

## Experimental System and Sampling Procedures

Three experiments were completed on separate days to investigate the formation and release of chloroform during routine use of commercial bleach in a residential washing machine. Recommended levels of soiled laundry whites, detergent, and domestic laundry bleach were used during each experiment. Air samples were collected to quantify formation and headspace accumulation of chloroform during wash cycles. Wash water samples were collected during two of the three experiments to quantify chloroform concentrations in the liquid phase following bleach addition. Additional samples were collected to quantify residual chlorine, total organic carbon (TOC), air and water temperatures, and pH.

Washing machine headspace samples were collected on Carbotrap 300 multi-bed adsorbent tubes (1/4 inch o.d., stainless steel with glass-lined inner walls) using SKC model 224-PCXR7 programmable air sample pumps calibrated using a primary flow standard, i.e. bubble flow meter. Sample flow rates were set to approximately 100 mL/min using a variable low flow control manifold. The Carbotrap tubes were characterized by three adsorbents in series, the last of which consists of a hydrophobic carbon molecular sieve necessary to avoid interferences caused by headspace water vapor competition for sorption sites, and the effects of condensation during tube desorption and sample analysis. The effectiveness of similar hydrophobic sorbents in humid atmospheres has been documented elsewhere.<sup>21</sup> Prior to their use, all adsorbent tubes were conditioned for four hours at 210°C with a charcoal purified helium flow of 30 mL/min per tube using a Tekmar model 5100 multi-tube conditioner. Following tube conditioning and sample collection, tubes were sealed using stainless steel Swagelock plugs with teflon ferrules, and refrigerated at 4 °C.

The experimental sampling arrangement is illustrated in Figure 1. A domestic automatic washing machine was located in a 3 x 3 x 2.5 m basement laundry room. The single door to the room was closed, and the room was not force-ventilated. Two air sample pumps were used throughout the experiments; one as an area sampler and one to acquire samples from the washing machine headspace. The area sampling pump was fitted with an adsorbent tube, and placed in the open room approximately 3 m away (diagonally opposite) from the washing machine, and at a height of 1.5 meters above floor level. It was used to collect samples before and during each experiment. The second pump was placed adjacent to the washing machine, and was fitted with adsorbent tubes only when sampling was required, i.e. during agitation of the wash water. The washing machine was filled to capacity (approximately 35 L) with warm tap water (28°C). All headspace samples were collected during agitation of the wash water by threading an adsorbent tube through a natural gap between the lid and the base of the machine (i.e., the lid was not raised during wash water agitation). In order to eliminate the possibility of variable water content, each experiment consisted of two sequential wash cycles (conditions) with individual headspace samples collected during each cycle. For each experiment, headspace samples were collected in series under the following conditions (sample times noted in parentheses):

- condition 1. above agitated wash water after the addition of 150 mL of commercial powdered laundry detergent (5 minutes), and
- condition 2. above the same water mixture after the addition of commercial bleach (5.25 % by mass) (3 to 12 minutes).

The washing machine lid was opened following each experimental condition, and closed at the beginning of each new condition. The same wash water was used throughout each of the two conditions, with drainage following the second condition (analysis with bleach addition). For two of the three experiments, wash water was not discharged to a laundry tub during air sampling. For

the second experiment, wash water was allowed to drain to a laundry tub after the aforementioned wash sequence (following condition 2 - bleach addition). Room air samples continued to be collected for 30 minutes following wash water drainage.

Wash water samples were collected in 100 ml plastic bottles immediately following each of the two wash conditions, and were used for TOC, residual chlorine, and pH quantification. Wash water samples were also collected at the end of the bleach wash cycles during experiments 1 and 3. Samples were collected in EPA-approved 40 ml glass vials with teflon-lined screw caps and zero headspace. Liquid samples were refrigerated at 4 °C immediately after collection.

Room and wash water temperatures were measured immediately prior to and during all experiments. Wash water temperature varied from 26-28°C during all experimental conditions. Room temperatures varied from 18 to 21°C.

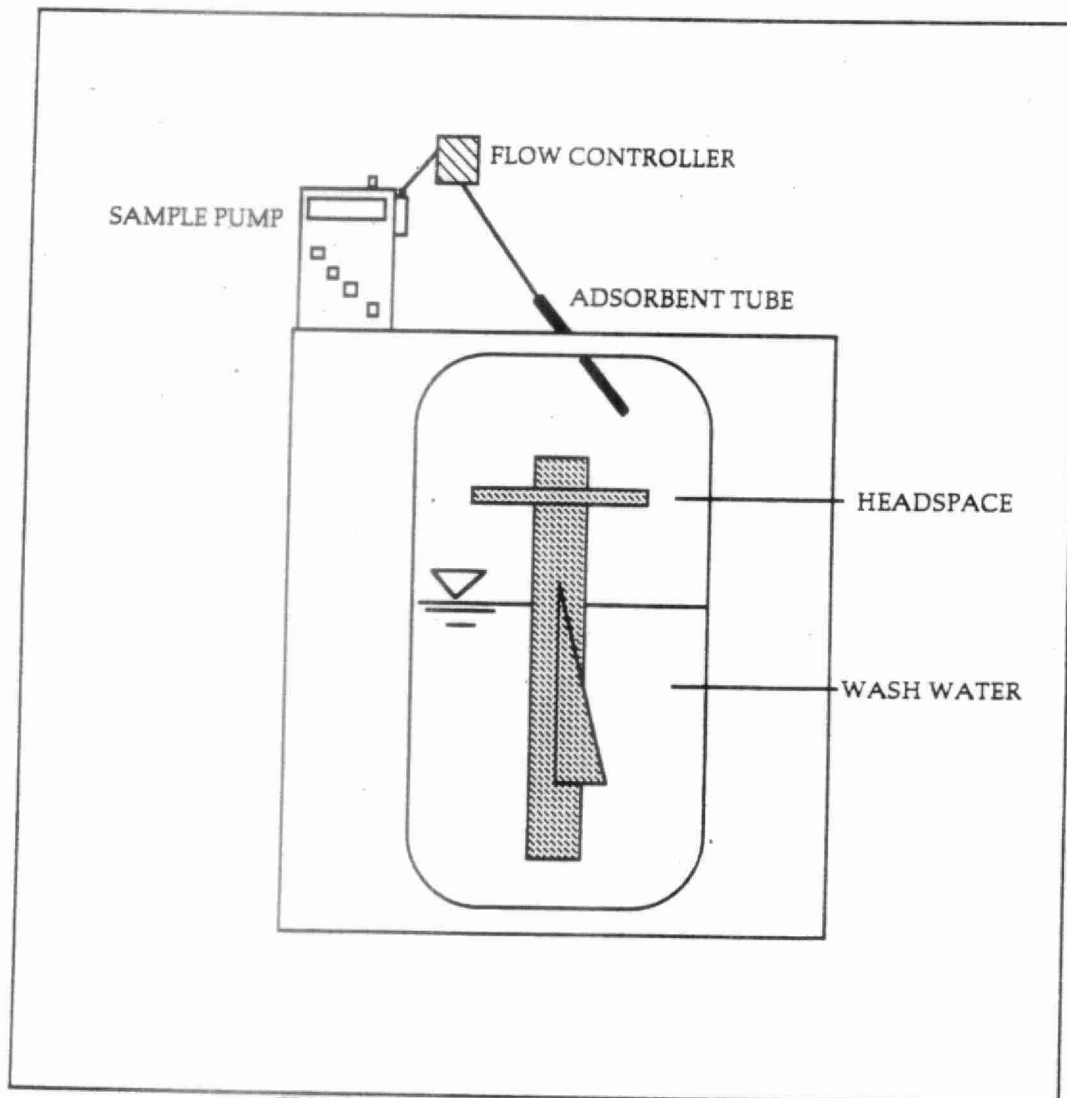


FIGURE 1. Headspace sampling arrangement.

## Sample Analysis

All adsorbent tubes and all glass-contained liquid samples (pre-concentrated by purging onto adsorbent tubes) were analyzed with a Tekmar LSC 2000 purge and trap (PAT), a Hewlett Packard 5890 Series II gas chromatograph (GC) equipped with a 30 m DB-5 capillary column (0.2 mm i.d. and 1  $\mu$ m film thickness), and a Hewlett Packard 5971 quadrupole mass spectrometer (MS) in the scan mode. The PAT cycle consisted of a 3 minute helium dry purge followed by a 2.75 minute desorb at 195 °C. The GC temperature conditions were: 24°C initial temperature, ramp at 40°C/min to 42°C, hold at 42 °C for 2.33 min, ramp at 10°C/min to 150°C, bake column for 3 minutes at 210°C. For each set of air samples, a three-point external calibration curve was completed for chloroform in the mass range of 20 to 500 ng per tube. Calibration curves were consistently characterized by  $R^2 > 0.999$ . The MS was tuned to be optimally responsive to volatile organic compounds, including chloroform.

Total residual chlorine was measured using the N,N-diethyl-*p*-phenylenediamine (DPD) ferrous titrimetric method as outlined in Standard Methods.<sup>22</sup> Total Organic Carbon analyses were completed at the University of Guelph's Land Resource Science Analytical Service Laboratory. Standard methods for TOC quantification were not used. Instead, TOC was quantified by analyzing a dried (pre-evaporated at 85 °C) aliquot of wash water sample in a Leco Carbon Determinator equipped with an induction furnace (i.e., by carbon dioxide analysis). Thus, it is possible that the actual reported TOC concentrations are slightly lower than actual TOC concentrations based on losses of some volatile organic carbon during the evaporation process. Finally, pH analyses were completed using standard combination (silver/silver chloride) pH electrodes with an Accumet model 925 pH meter.

## RESULTS

A summary of wash water conditions at the end of each experimental cycle is provided in Table II. Values of pH ranged from 9.2 to 9.7 following the introduction of detergent and bleach. Total organic carbon concentrations were consistently between 135 - 179 mg/L following the addition of detergent to wash water. Those compounds which make up the reactive (chloroform precursor) fraction of TOC were not identified and have not been reported in previous literature.

Total residual chlorine concentrations were obtained for experiments 1 and 3, and are reported in Table II as mg/L ( $\text{Cl}_2$  equivalents). The values listed in Table II represent greater than a 90% reduction of initial gravimetric  $\text{Cl}_2$  addition to wash water. This indicates that a substantial fraction of the chlorine reacts quickly in the wash water, with the potential for rapid formation of chloroform and other halogenated organic compounds.

Headspace and wash water chloroform concentrations are presented in Table III. Liquid samples were collected only for experiments 1 and 3. For experiments 2 and 3, two headspace samples were collected following the addition of bleach. The time intervals over which gas samples were collected are indicated in parentheses.

The ranges of wash water chloroform concentrations were fairly reproducible between experiments 1 and 3, and were substantially higher than the less than 10  $\mu\text{g/L}$  of chloroform typical of Guelph drinking water (chlorinated groundwater). Thus, the data presented in Table III clearly



indicate the formation of chloroform in washing machine wash water. Washing machine headspace samples were also reproducible. All three experiments yielded approximately  $1 \text{ mg/m}^3$  of chloroform accumulation during the first five minutes following bleach addition. These concentrations were a factor of 15 or more higher than headspace concentrations prior to bleach addition, clearly indicating rapid chloroform formation followed by transfer from the wash water to overlying air.

TABLE II. Summary of wash water conditions.

Experiment	pH	TOC (mg/L)	Residual chlorine (mg/L)
1.w+c+d	9.4	135	-
1.w+c+d+b (0 - 5 min)	9.6	174	16
2.w+c+d	9.5	142	-
2.w+c+d+b (0-5 min)	9.7	179	-
2.w+c+d+b (5-17 min)	9.7	172	-
3.w+c+d	9.2	162	-
3.w+c+d+b (0-3 min)	9.3	-	-
3.w+c+d+b (3-6 min)	9.2	157	12

w = water (35 L)  
c = clothes (4 kg)  
d = detergent (150 ml of powder)  
b = bleach (150 ml of 5.25 % NaOCl)

Headspace chloroform concentrations did not reach equilibrium with underlying wash water during the experiments. In fact, using a dimensionless Henry's law constant of 0.15 for chloroform, the equilibrium liquid concentration associated with measured headspace concentrations ranged from 6 to  $11 \text{ mg/m}^3$ . These equilibrium values were only 3 to 5% of chloroform concentrations measured in wash water, and suggest that for all intents and purposes the transfer of liquid-to-gas can be reasonably modeled as an infinite ventilation (zero gas concentration) process for short (5 to 15 minute) wash cycles. This makes the earlier caveat associated with chloroform-to-radon transfer efficiencies of lesser importance, and supports McKone's approach of surrogate compound extrapolation for washing machines.

Table III indicates that chloroform was above detection limit in laundry room air during the second experiment. This was the only experiment during which time wash water was discharged into an open tub/sink. Even more important than the formation of small quantities of chloroform in room air is the fact that insignificant amounts of chloroform appeared to accumulate in room air when the washing machine lid was closed. This suggests that the two primary mechanisms for chloroform emissions during laundry activities are 1) rapid headspace turnover following the opening of a machine lid, and 2) stripping of chloroform from chlorinated wash water during drainage to an adjacent laundry tub or sink.

TABLE III. Experimental chloroform concentrations.

Experiment	Chloroform concentration (mg/m <sup>3</sup> )	
	headspace or room air	wash water
1 (room air)	< 0.003	
1.w+c+d	<0.001	
1.w+c+d+b (0-5 min)	0.9	170 - 210
2 (room air)	0.03	
2.w+c+d	0.07	
2.w+c+d+b (0-5 min)	0.68	
2.w+c+d+b (5-17 min)	1.6	NC
3 (room air)	< 0.001	
3.w+c+d	0.02	
3.w+c+d+b (0-3 min)	0.30	
3.w+c+d+b (3-6 min)	1.0	150 - 230

w = water (35 L)  
c = clothes (4 kg)  
d = detergent (150 ml of powder)  
b = bleach (150 ml of 5.25 % NaOCl)

NC = not completed

## SUMMARY AND CONCLUSIONS

This paper provides an overview of a screening study completed to ascertain the potential for chloroform generation in household washing machines. The following observations and conclusions were made based on preliminary (phase I) research:

1. Laundry wash water contains surrogates necessary for the formation of chloroform.
2. Chlorine reacts quickly in washing machines, in part to form trihalomethanes such as chloroform.
3. Significant levels of chloroform appear to be generated following the addition of commercial bleach to wash water.
4. During wash cycles, the gas-liquid mass transfer process associated with chloroform transfer from wash water to headspace does not reach equilibrium.
5. The two primary mechanisms for chloroform emissions during laundry activities are likely to be 1) rapid headspace turnover following the opening of a washing machine lid, and 2) stripping of chloroform from chlorinated wash water during drainage to an adjacent tub/sink.



Based on the results of the preliminary (screening) study presented in this paper, it appears that laundry activities can be major contributors to chloroform concentrations in households that use bleach containing sodium hypochlorite. However, these results are not sufficient in scope to determine the relative importance of washing machines as sources of chloroform emissions to indoor air, and conclusions regarding the need for concerns related to such emissions are not possible at this time.

Additional studies are warranted to assess the significance of chloroform and other volatile compounds which are emitted during laundry activities, and to better understand the basic physical and chemical mechanisms associated with chloroform formation and gas-liquid mass transfer in household washing machines. Phase II of this research is currently underway. It is focussing on headspace gas-dynamics, gas-liquid mass transfer between wash water and the overlying headspace, and other halogenated organics which form during the use of sodium hypochlorite.

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## NOTE TO EDITORS

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# **Fate of Volatile Organic Compounds in Wastewater Collection Systems**

## **Volume VII: Formation of Chloroform - Post-Discharge**

Kimberley O'Neill  
M.Sc. thesis

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

September, 1994

FORMATION OF CHLOROFORM IN UNTREATED MUNICIPAL  
WASTEWATER

a Thesis

Presented to

The Faculty of Graduate Studies

of

The University of Guelph

by

KIMBERLEY O'NEILL

In partial fulfilment of requirements

for the degree of

Master of Science

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## ABSTRACT

### FORMATION OF CHLOROFORM IN UNTREATED MUNICIPAL WASTEWATER

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University of Guelph, 1993

Advisor:  
Dr. R. Corsi

Chlorine may be introduced to municipal sewer systems from industrial discharges as well as from a wide range of sources including residential households, laundries and low energy dishwashers used in restaurants. Chlorination of waters containing organic substances leads to the formation of chlorinated organics, in particular trihalomethanes (THMs). Trihalomethanes are a group of volatile and potentially carcinogenic compounds which can be stripped from sewers to the atmosphere. Laboratory studies were completed to assess whether trichloromethane (chloroform) formation due to bleach discharges contributes significantly to VOC loadings in municipal wastewater. Untreated municipal wastewater was spiked with chlorine concentrations ranging from 2 to 200 mg/L  $\text{Cl}_2$ . The formation of chloroform was found to be directly proportional to chlorine dose. Formation factors were observed to range from 0.4 to 4.3  $\mu\text{g}$  of chloroform per mg of chlorine spiked. These values were comparable to formation factors observed in previous studies using untreated and partially treated wastewaters. The formation factor values were coupled with estimated chlorine use rates in the City of Guelph to predict average chloroform formation values. Chloroform formation in Guelph sewers was found to be small relative to chloroform levels in potable drinking water.

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## 1.0 INTRODUCTION

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Many studies have been completed to assess the formation of chloro-organics in treated wastewater following chlorination (Cooper *et al.*, 1977; Glaze *et al.*, 1979; Helz *et al.*, 1985; Stenstrom *et al.*, 1987; Van Leeuwen and Rossum, 1990). Trihalomethanes are found in virtually all chlorinated water supplies and generally occur at the highest concentrations relative to other waterborne chemical contaminants (Reiches and Wilkins, 1983). They are confirmed water chlorination by-products. Chloroform (a trihalomethane) is classified by the United States Environmental Protection Agency as a probable human carcinogen (Federal Register, 1986). The Registry of Toxic Effects of Chemical Substances (U.S. Department of Health, Education and Welfare, 1975) states that systemic toxic effects are produced from chronic exposure by ingestion to chloroform at concentrations as low as 10 mg/L. The CRC Handbook, 1984 states that the limit for human exposure to chloroform by inhalation is 50 ppm (by volume) and NIOSH (1990) sets a short term (60 minute) airborne exposure limit to chloroform of 2 ppm (9.78 mg/m<sup>3</sup>).

Natural sources of chloroform, e.g. the oceans, account for a background concentration of chloroform in the atmosphere of approximately 32 parts per trillion (ppt) (Roberts, 1980). Chloroform concentrations of 5,000 to 10,000 ppt have been recorded in urban atmospheres.

Few studies have been completed to assess trihalomethane formation when

untreated wastewater is chlorinated. Chlorination of raw wastewater can occur when bleaches (usually in the form of sodium hypochlorite) from residential laundry, commercial laundry and dishwashers used in restaurants are discharged to sewer systems. It has been shown in previous studies that chlorine addition to waters containing humic substances, i.e. wastewaters and surface waters, causes the formation of trihalomethanes (Kavanaugh *et al.*, 1980). It has, until recently, been assumed that chlorine entering municipal sewers would not cause formation of significant concentrations of THMs because of relatively high concentrations of ammonia present in untreated wastewater and the high reaction rate of chlorine with ammonia compared to those of other wastewater constituents (Amy *et al.*, 1984). However, few studies have been completed to verify this assumption based on estimated chlorine discharges to sewers.

### **1.1 Purpose**

This study provides estimates of the extent of chloroform formation when commercial bleaches containing sodium hypochlorite are discharged to municipal sewers. An assessment of the relative importance of in-sewer formation as a source of chloroform in wastewater is also completed. Specific objectives include:

1. quantification of chloroform formation factors,
2. identification and quantification of the effects of wastewater characteristics on chloroform formation factors,

3. determination of the relative significance of in-sewer chloroform formation values relative to other known sources.

Chloroform formation due to chlorination of raw wastewater has only recently been examined. Previous studies concentrated on partially or fully treated wastewater. This study attempts to quantify chloroform formation in mainly residential raw wastewater over a limited range of wastewater characteristics.

## 1.2 Scope

Wastewater was collected from the headworks of the Guelph Wastewater Treatment Facility, and chloroform formation assessments were completed within two hours. The range of wastewater characteristics was limited, as the wastewater was primarily from residential sources. Characteristics of the wastewater were not intentionally altered.

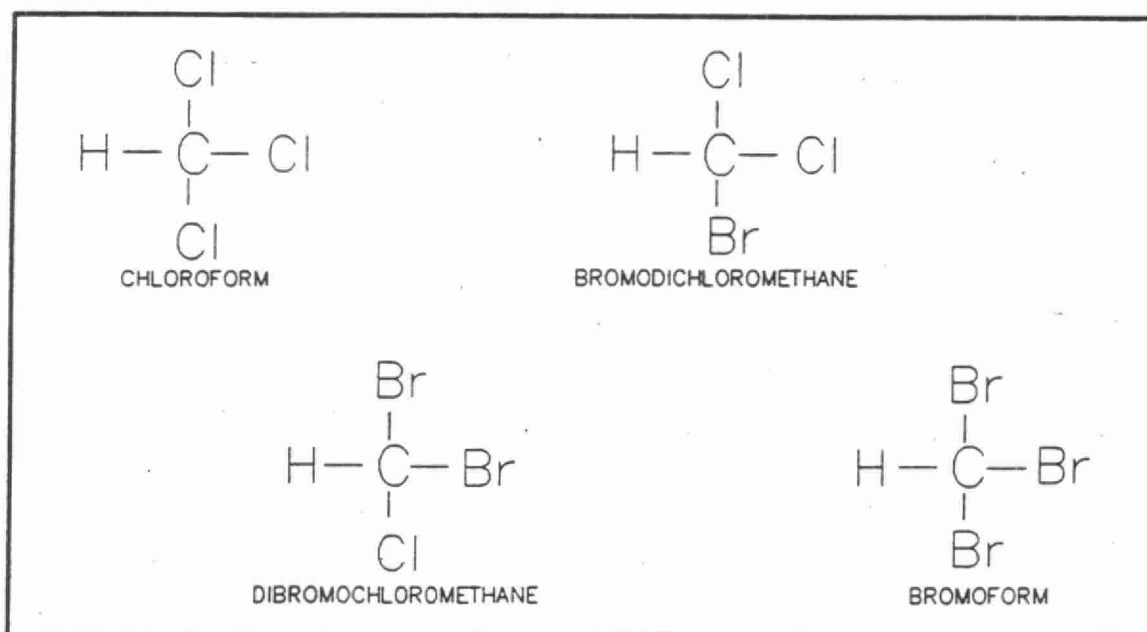
Chlorine doses were based on chlorine discharge rates calculated from previous studies as well as a market survey completed within Guelph. The chlorine doses ranged from 0 mg/L to 100 mg/L. Actual discharge rates of chlorine to the sewer system were not tested in the field due to time restrictions.

An assessment of the precursor to chloroform formation upon chlorination was not completed. Total organic carbon (TOC) analyses were attempted to relate organic content to chloroform formation factors. The TOC analyses were not successful as the equipment utilized by the laboratory completing the analyses was not appropriate for wastewater analysis. Therefore, no useful information was

gained from the TOC analyses.

An assessment of wastewater characteristics was completed prior to each chloroform formation experiment. Wastewater characterization included pH, ammonia concentration and total and volatile suspended solids concentrations.

The compounds of interest to this study are the four trihalomethanes shown in Figure 1.



**Figure 1     Trihalomethanes Examined for this Study**

Formation of trihalomethanes in untreated wastewater is dependent on several factors, including chlorine discharge quantities, competing reaction mechanisms with ammonia and other inorganic compounds, concentrations of organic precursors, and wastewater characteristics that affect formation chemistry.

This chapter provides background into the processes involved with

chloroform formation, consumption of free chlorine in processes other than those leading to chloroform formation and sources of chlorine discharge to sewer systems. A review of chloroform formation factors reported by other researchers is also provided.

## **2.1 Sources of Chlorine Discharge to Sewers**

Chlorine (in the form of sodium hypochlorite) is widely used in domestic and commercial practices. Its uses range from household laundry and cleaning to commercial and institutional laundries to surface cleaning in industrial and commercial locations. A major source of chlorine discharge to sewer systems is from low energy dishwashers (Bridgman, 1992). Because these dishwashers use lower water temperatures for cleansing, they utilize higher concentrations of sodium hypochlorite in the rinse water to ensure disinfection. The chlorination of these waters produces various halogenated organics including trihalomethanes (THMs) (Chou, 1990; Gurol and Itell, 1989; Helz *et al.*, 1985; Kavanaugh *et al.*, 1980)

Table 1 shows various potential sources of chlorine which can enter a sewer system. The associated pre-discharge chlorine concentrations (i.e., before dilution occurs) do not take into consideration any loss of chlorine due to reactions previous to those in the sewer system.



**Table 1: Chlorine Usages and Recommended Concentrations for Commercial and Residential Practices (Bridgman, 1992).**

Source	Recommended Chlorine Concentrations
Low temperature dishwashers	100 ppm
Commercial glasswashers	100 ppm
Manual warewashing	100 ppm
Mop and pail solutions	300 ppm
Sanitizing solutions	200 ppm
Chlorinated detergent used in high energy dishwashers	50 ppm
Commercial/institutional laundry	70 ppm
Residential laundry and cleaning/disinfection	200 ppm

Table 1 does not cover uses of chlorine for industrial practices. Industrial uses are extensive and range from cleaning solutions to bleaching of products. Industrial sources of chlorine were not considered in this study.

## **2.2 Chlorine use Rates for the City of Guelph**

Chlorine use rates are typically based on market (sales) data for a particular city or region. For example, Rogozen *et al.* (1988) reviewed a market survey which led to estimates of  $6.8 \times 10^7$  kg of sodium hypochlorite (as NaOCl) used in the United States in domestic laundry bleaches alone on an annual basis. This

translates to an average chlorine ( $\text{Cl}_2$ ) use rate of 1.3 kg/household/year or 0.4 kg/person/year. Bleach usage data for other consumptive categories, e.g. industrial uses and low-energy dishwashers in restaurants, were not readily available. It was therefore estimated that there would be at least an annual  $\text{Cl}_2$  equivalent loading of 23,000 kg for a city the size of Guelph, Ontario (population: 85,000, 5 persons/household). It should be recognized that a fraction of the aforementioned loading would react prior to entering a sewer system, e.g. in washing machines, and that free chlorine consumption prior to discharge can be large (Corsi *et al.*, 1992).

An estimate of in-sewer chloroform generation can be obtained by coupling total chlorine use rates with chloroform formation factors (FF –  $\mu\text{g}$  chloroform/mg chlorine dosed) in raw wastewater. For this study, chloroform formation factors were calculated experimentally, and chlorine loadings were estimated by extrapolation of the U.S. market survey described above, along with a market survey completed for the City of Guelph.

As part of this study, a bleach distributor was contacted and agreed to provide data regarding sodium hypochlorite sales in Guelph (Bridgman, 1992). These data were estimated from total sales of bleach products in the area. There were an estimated 70 low temperature (low energy) dishwashers in Guelph that used 6.4 L/cycle at a recommended concentration of 100 ppm sodium hypochlorite; the number of cycles per day being dependent on need (20 to 40 runs). Another 30 dishwashers were estimated to have used 5.7 L/minute at 100

ppm sodium hypochlorite. The average run time of the rinse cycle (where the sodium hypochlorite is used) for these dishwashers was 60 minutes/day. Further estimates were made for manual washing of dishes and mop and pail solutions used for washing floors (See Appendix C for actual values used). It was estimated that 2,000 kg of chlorine were consumed per year for these uses, approximately 10% of the domestic consumption described by Rogozen *et. al.* (1988).

A market survey, at two large retail grocery stores in the Guelph area, was completed in order to estimate sales of chlorine-containing bleach on an annual basis. It was estimated that, on average, 1,800 L of 6% to 12% chlorinated bleach solution was sold per week in Guelph with an average of 15,000 customers. These values were then extrapolated to the population of Guelph (85,000). A value of 500 cubic meters of pure chlorinated bleach was estimated to be consumed on a yearly basis, which is equivalent to 15,000 kg/ year of chlorine ( $\text{Cl}_2$ ). This value is close to the estimated 23,000 kg/year based on Rogozen's (1988) data.

A total of  $1.7 \times 10^7$  cubic meters of wastewater was treated at the Guelph Wastewater Treatment Facility in 1992. Using the bleach consumption estimates described above and the City of Guelph wastewater flow rates, it was estimated that there should be 1.0 to 1.5 mg/L of chlorine in raw municipal wastewater from residential uses alone on an annual basis.

Bridgman (1992) stated that the recommended concentration of chlorine in low energy dishwashers was 100 mg/L. The consumption of chlorine in

dishwashers due to reaction is unknown at this point in time. However, it was assumed that no reaction in dishwashers or washing machines occurred and that all of the free chlorine used was discharged to the sewer system. Values ranging from 0 to 100 mg/L of chlorine in the sewer system were considered to represent the range of chlorine concentrations that could potentially occur in various areas of a sewer system typical of the City of Guelph.

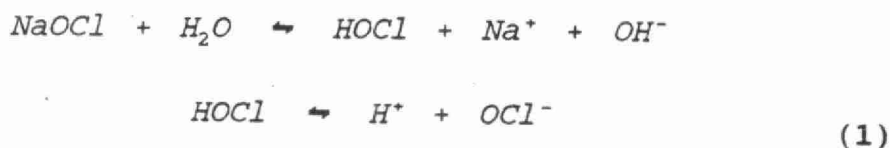
These values are conservative estimates as no correction is made for consumption due to reactions while cleaning. However, the integrated values of 1.0 to 1.5 mg/L are likely to be low locally, as solutions entering a sewer system cause immediate levels of chlorine to be considerably higher at some locations. Although this should not significantly affect the total mass of chloroform formed in sewers, it has an impact on the locations where highest chloroform emissions from sewer systems occur, i.e. leading to possible variations in chloroform concentrations in sewer offgas streams at different exhaust locations.

## **2.3 Reactions of Chlorine in Wastewater**

The primary constituents of wastewater which consume chlorine are ammonia, inorganic compounds and organic constituents (including trihalomethane precursors). Chlorine may also adsorb to and react with suspended solids in wastewater. The following sections describe reactions of these compounds with chlorine and other processes which affect the reaction mechanisms of chlorine to form chloroform in untreated wastewater.

## Dissociation

Chlorine applied to water in its elemental form or as 'sodium hypochlorite initially undergoes hydrolysis to form "free chlorine" consisting of aqueous molecular chlorine ( $\text{Cl}_2$ ), hypochlorous acid ( $\text{HOCl}$ ) and hypochlorite ion ( $\text{OCl}^-$ ). Equation set 1 shows these reactions.

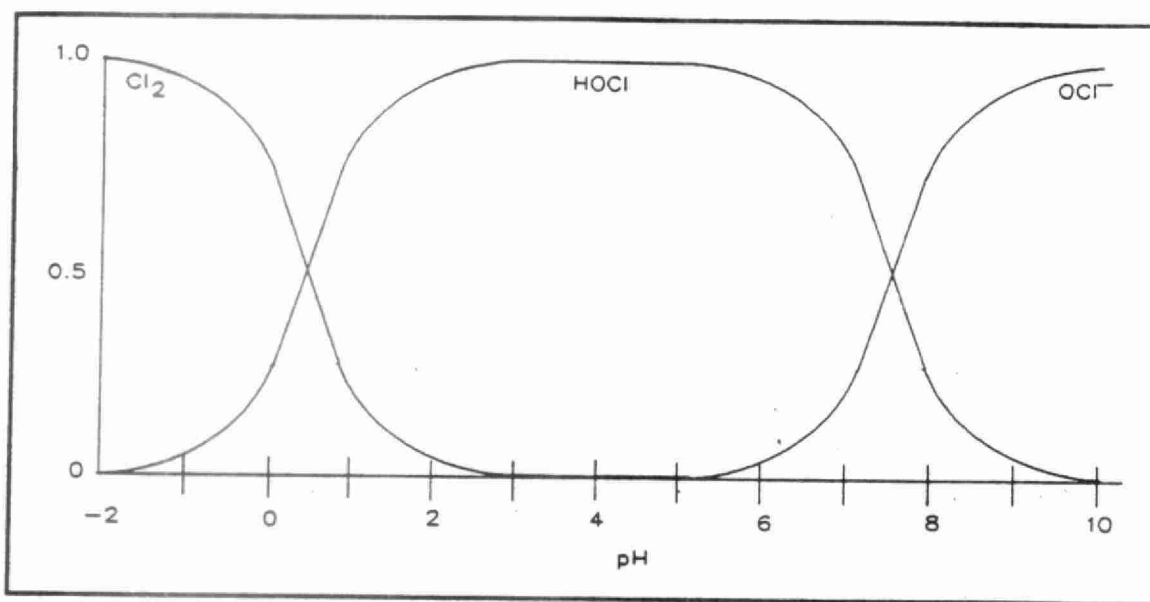


### **Low pH**



This hydrolysis reaction is very rapid and goes to completion in less than one second (Stenstrom *et al.*, 1987). The relative proportion of free chlorine forms is pH and temperature dependent. At the pH of most natural waters and municipal wastewaters (pH 6 to 9), hypochlorous acid and hypochlorite ion predominate (see Figure 2).

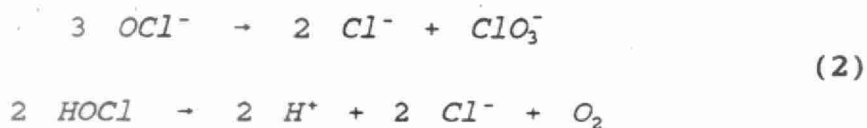
Stenstrom *et al.* (1987) stated that reactions of chlorine with ammonia come to virtual completion at pH 8.3 in less than one second at high ratios of chlorine to ammonia. It has also been shown that as pH increases trihalomethane formation increases (Peters *et al.*, 1980). Therefore in the pH range of most municipal wastewaters (6 to 9), chlorine is thought to be in its most reactive state.



**Figure 2 Sodium Hypochlorite Dissociation**

### Decomposition

Decomposition of hypochlorous acid and the hypochlorite ion will occur over time if these species do not react with other constituents in water (see equation set 2).



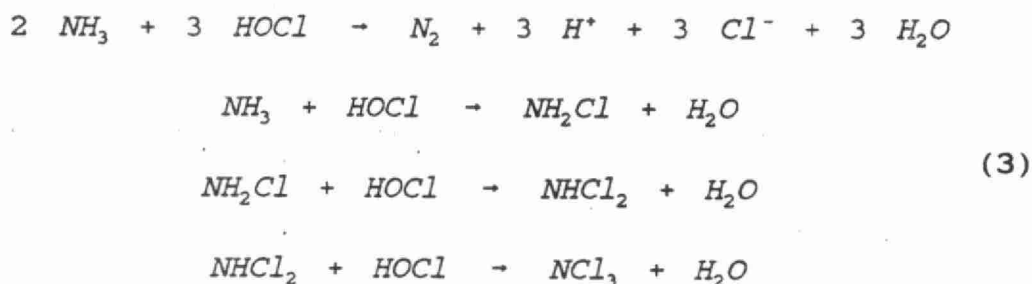
Because the reactions of chlorine with ammonia and/or inorganic constituents are very rapid, decomposition reactions were not of concern in this study.

### Reactions with Ammonia

Aqueous ammonia can exist in two forms depending on pH. The  $\text{pK}_a$  of

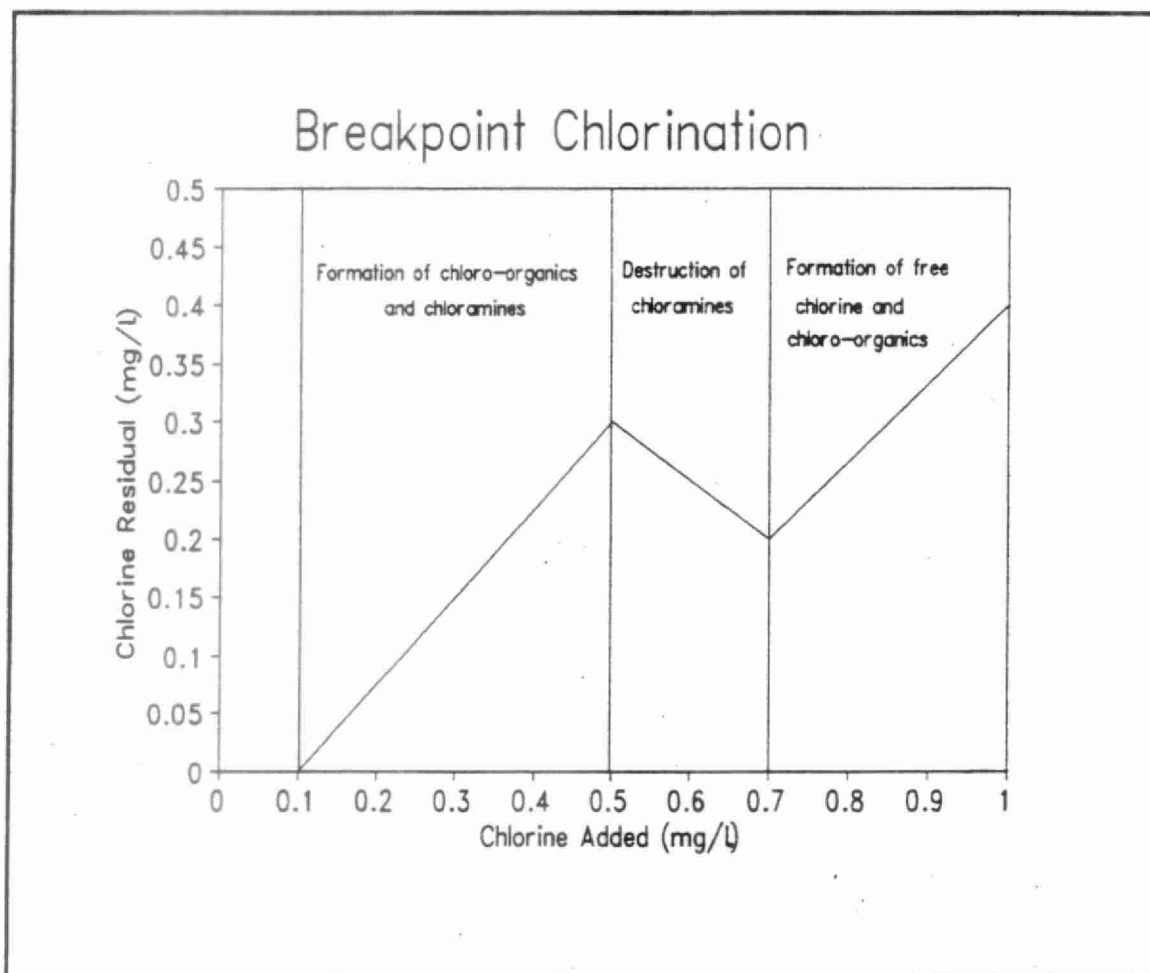
aqueous ammonia is 9.23 (CRC Handbook of Chemistry and Physics, 1984). This value is for ammonia solutions at 20°C and the full range of ammonia concentrations. This implies that at 20°C the majority of ammonia will be in the form of  $\text{NH}_4^+$  if the pH of the solution is below 9.23 or in the predominant form of  $\text{NH}_3$  if the solution is above pH 9.23.

Chlorine reacts rapidly with ammonia present in wastewater to form monochloramine ( $\text{NH}_2\text{Cl}$ ), dichloramine ( $\text{NHCl}_2$ ), and nitrogen trichloride ( $\text{NCl}_3$ ). These compounds are all forms of combined chlorine (see equation set 3), and collectively make up a group of compounds known as chloramines.



The rates of formation of these compounds and the ratio of mono to dichloramine are dependent on the pH of the wastewater and the concentration of hypochlorous acid (Stenstrom *et al.*, 1987). Low pH values favour the formation of monochloramine and higher pH values the formation of dichloramine. However, the first combined residual to form is monochloramine, followed by dichloramine at rising chlorine concentrations for all pH values. As the concentration of chlorine with respect to ammonia increases, chloramines break down to form nitrogen gas. The point at which all of the combined chlorine (in the form of chloramines) has reacted to form nitrogen gas or a variety of nitrogen-containing chlorine-free

products is called 'breakpoint'. After breakpoint, the addition of chlorine produces only free residual chlorine, i.e.  $\text{Cl}_2$ ,  $\text{OCl}^-$  and  $\text{HOCl}$  (see Figure 3).



**Figure 3 Breakpoint Chlorination**

The observed stoichiometry to reach breakpoint in secondary treated wastewater effluent is generally 3 moles of chlorine as  $\text{Cl}_2$  per 2 moles of ammonia



(Snoeyink and Jenkins, 1930). This ratio may increase with increased concentrations of inorganic compounds other than ammonia in untreated wastewater (See Section 2.2). This is referred to as increasing the "chlorine demand".

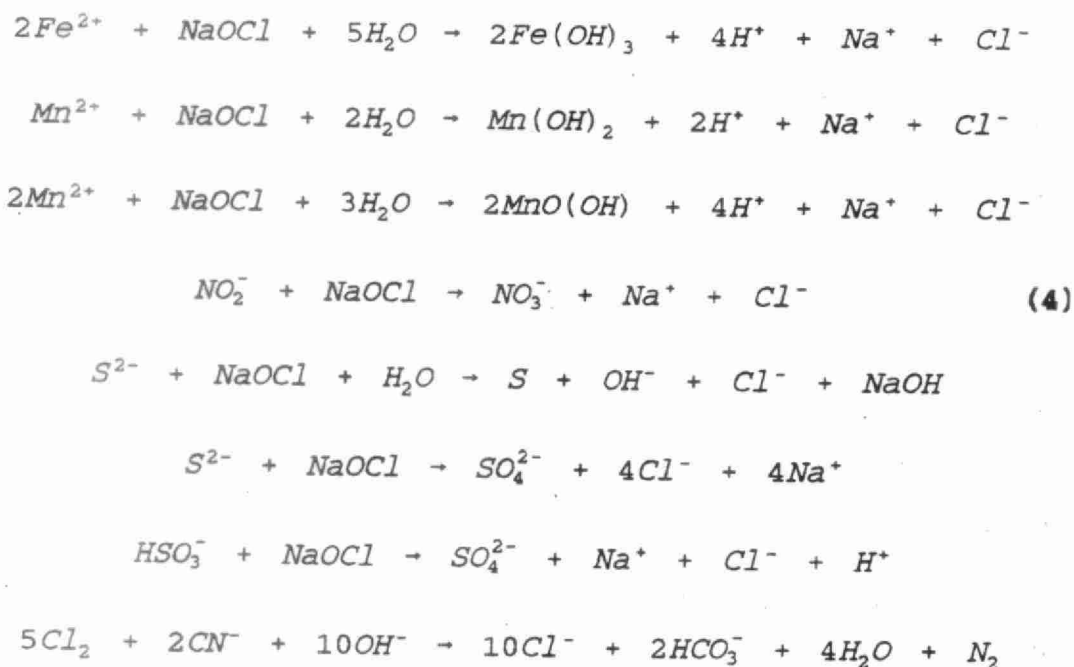
The reaction rates for chloramine formation are generally rapid, but less than those for chlorine dissociation (Stenstrom *et al.*, 1987). At pH 2 it may take as long as 7 minutes for these reactions to come to completion (Stenstrom *et al.*, 1987). In wastewater, it has been noted that monochloramine reactions are the fastest at pH 8.3, and are 99% complete in one second for ratios of ammonia : chlorine concentrations (mol/L) of 1:20 (Snoeyink and Jenkins, 1980). This level of chlorine concentration is significantly higher than those observed in most raw municipal wastewaters. However, the results clearly indicate rapid chlorine consumption in wastewater.

On average, ammonia concentrations in Guelph wastewater range from 10 to 40 mg/L. In other areas, concentrations of ammonia in untreated municipal wastewater can be as high as 100 mg/L or more (Dore *et al.*, 1982).

### **Reaction with Inorganic Constituents**

For all intents and purposes, hypochlorite reacts instantaneously with certain inorganic compounds at pH values near and above neutrality (Snoeyink and Jenkins, 1980). Thus, there is an immediate inorganic demand for free chlorine in wastewater. The extent of the demand is highly dependent on the specific

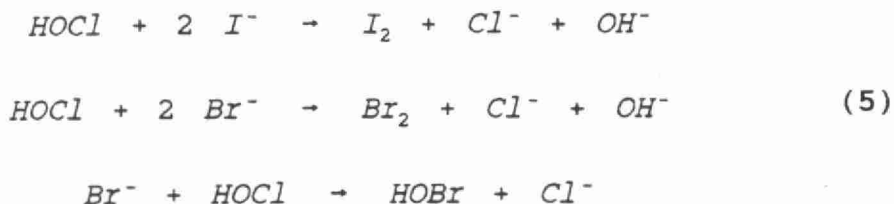
wastewater, i.e. concentrations of specific inorganic species. Furthermore, the importance of the inorganic demand is magnified at low chlorine doses in which a significant fraction of chlorine can be "scavenged" by inorganic species. Equation set 4 illustrates numerous inorganic compounds that react with chlorine in raw wastewater. Equation set 4 also illustrates inorganic species commonly observed in municipal wastewaters. These include iron, manganese, sulfide, sulfate, nitrite and cyanide.



### Reactions with other Halogens

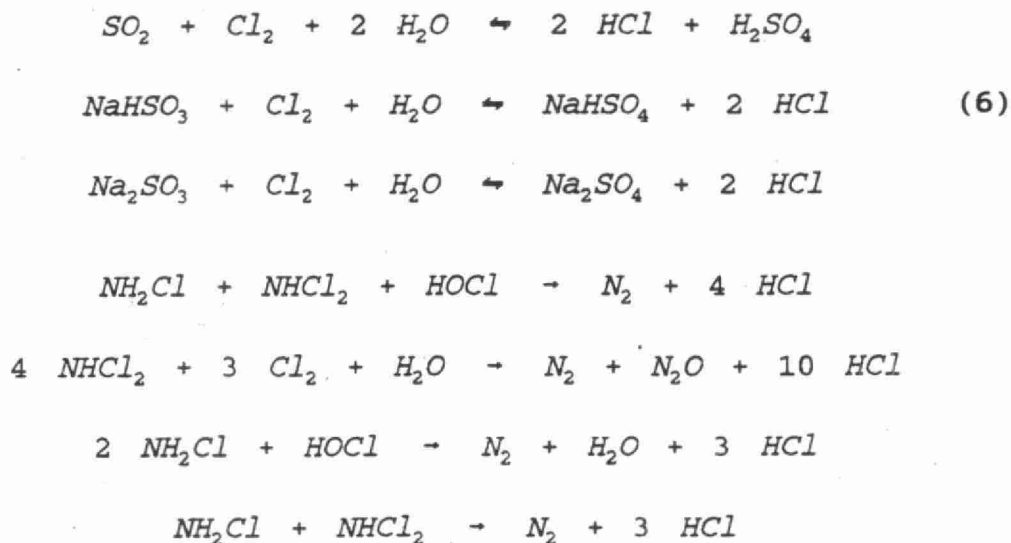
Chlorine reactions with other halogen ions are shown in Equation set 5. The reaction of sodium hypochlorite with iodide is used for the determination of residual chlorine and chloramines in samples. Therefore, other halogens present in the wastewater will cause interference when a chlorine concentration

determination is attempted. The procedure for determination of chlorine concentration may be found in the experimental methodology section.



### Dechlorination

Examples of dechlorination reactions are provided in Equation set 6. These reactions illustrate how sodium sulfite or sodium thiosulfate may be used to quench the reactions of chlorine in wastewater.



## **2.4 Trihalomethane Formation**

The reactions described in section 2.3 illustrate how sodium hypochlorite would react with various constituents of wastewater. These reactions will have an effect on the formation of trihalomethanes. The individual effects of wastewater parameters on the formation of trihalomethanes are described below.

### **2.4.1 Factors Affecting Chloroform Formation**

Many factors affect the formation of trihalomethanes in wastewater including chlorine concentration, temperature, pH, ammonia concentration, type of precursor and reaction time (Amy *et al.*, 1984; Dore *et al.*, 1982; Urano *et al.*, 1983).

#### **Chlorine Concentration**

Trihalomethane formation increases with increasing chlorine dose (Amy *et al.*, 1984; Dore *et al.*, 1982; Peters *et al.*, 1980; Urano *et al.*, 1983). It has been stated that the determining factor for the formation of chloroform is the quantity of chlorine available for the precursors, which depends on the relative reaction rates of the precursors and other reductive compounds (Dore *et al.*, 1982).

Chlorine entering the sewer system may be at concentrations ranging from 0 to greater than 100 mg/L (See Table 1) (Bridgman, 1992). As the chlorine discharge enters a sewer system it will be diluted to varying concentrations depending on the flow of wastewater and discharge streams. Thus, chlorine concentrations within a sewer system will not be spatially uniform. Chlorine dose

rates also vary temporally, as commercial and residential laundries use different quantities of chlorine depending on the season. During winter months, less chlorine is consumed than during the summer months.

### **Temperature and pH**

Trihalomethane formation in water will increase as temperature increases and pH is raised (Standard Methods, 1989). It has been stated that trihalomethane formation reaches a maximum at pH 8.3 (Snoeyink *et al.*, 1980). Conversely, it has also been stated that THM formation rate constants increase three fold for each unit increase in pH (Kavanaugh *et al.*, 1980).

Dore *et al.* (1982) studied the effect of pH on chloroform formation using three different precursors; resorcinol, acetylacetone and acetone. It was found that for each of the precursors, chloroform formation reached a maximum at different pH values. For resorcinol and acetylacetone, the maximum was reached at close to neutrality but was over pH 12 for acetone. This implies that, depending on the precursors to chloroform formation present in the wastewater (i.e. the type of wastewater), pH may have varying effects on chloroform formation.

### **Ammonia**

Amy *et al.* (1984) stated that ammonia occurring naturally, or added intentionally to provide chloramine disinfection, exerts a free chlorine demand and reduces THM levels since chloramines do not react to form THMs. However,

Cooper *et al.* (1977) stated that chloramines would still react to form chloroform but at rates much slower than free chlorine. Chow and Roberts (1981) reported that chlorine produced halogenated by-products in both the presence and absence of ammonia, but more organohalogens were formed in nitrified (nitrogen reduced) wastewater because chlorine is more reactive when it is not in its combined form.

Topudurti and Hass (1987) reported that the concentration of chloroform formed, when monochloramine was the chlorinating agent, was two orders of magnitude less than the concentration of chloroform formed when free residual chlorine was the chlorinating agent. It was stated that monochloramine could still produce chloroform in concentrations that could pose a health hazard.

These influences in chloroform formation will not be addressed in this paper due to the scope of experimentation. Only the effect of chlorine dosage on chloroform formation factors will be addressed.

#### **2.4.2 Precursors to Chloroform Formation**

The fact that trihalomethanes are present in nearly all chlorinated water supplies has led to the belief that the precursor to THM formation is present in all natural waters and wastewaters. Humic substances are virtually ubiquitous to natural waters and are a complex assembly of decayed plant and soil materials. Humic acids are substances which arise principally from the soluble fraction of wood tissues, by dissolution or dispersion of decomposition products of decaying wood or leaves, and by leaching of soluble components from soil organic matter

(Chou, 1990). It has been stated that polyhydroxyaromatic structures such as resorcinol and humic acids are probably the main precursor to THM formation (Dore *et al.*, 1982; Rook, 1976). They have been the focus of many studies as primary precursors to THM formation. However, there are still a number of other compounds which are capable of THM production.

Stenstrom *et al.* (1987) observed that chlorophyll, algal extracellular products and algal biomass are capable of forming THMs on contact with aqueous chlorine. Concentrations of THMs formed from these compounds were comparable to those formed by humic substances. It was also shown that phenols, ketones and a wide range of other simple organic compounds are capable of chloroform formation. However, because of the relatively low concentrations of THMs formed by these simple organics, they are not considered to be major THM precursors in untreated wastewater. Furthermore, byproducts of algal growth are not observed in dark sewer environments.

Kavanaugh *et al.* (1980) reported that humic acids showed the highest rate of formation of THMs compared to other organic constituents found in surface and wastewaters. They also stated that the rate of THM formation may depend primarily on the TOC level rather than on the type of humic substance present in the water.

Scully *et al.* (1984) completed studies on the formation of THMs using various types of proteins. The compounds studied were; bovine serum albumin, pepsin, rennin, cytochrome c and humic acid (molecular weight unknown).

Solutions of each of the proteins were made to carbon content of 2 to 3 mg/L and chlorinated at 20 mg/L  $\text{Cl}_2$ . It was found that the chloroform yield produced by the proteins of widely varying structure and molecular weight were quite similar. However, they all gave about one-half the chloroform yield of humic acid.

Chambon *et al.* (1983) reported that when urine was chlorinated at levels of 200 mg/L ( $\text{Cl}_2$ ) the chloroform formation yield was 3,000  $\mu\text{g/L}$ . These levels are an order of magnitude greater than most formation factors cited for wastewater. Upon further examination, Chambon *et al.* (1983) separated the various fractions of urine and found that, in the fraction containing acidic ethers, 2,900  $\mu\text{g/L}$  of chloroform was formed. An additional 115  $\mu\text{g/L}$  was formed in the fraction containing alkaline ethers, and 82  $\mu\text{g/L}$  in the remaining fractions (Chambon *et al.*, 1983).

Topudurti and Hass (1987) studied chloroform formation in the presence of ammonia before breakpoint chlorination (i.e. at  $\text{Cl}_2:\text{NH}_3 < 2:3$ ). They showed a direct correlation between the consumption of phloroacetophenone (PAP), which is a polyhydroxyaromatic structure or humic substance, and the formation of chloroform. The following reaction was presented:



It was reported that the reaction was only feasible if the molar ratio of chlorine to PAP was greater than eight.



### 2.4.3 Chloroform Formation Studies

A summary of formation factors found in various studies using different types of waters and wastewaters is provided in Table 2. Existing literature indicates formation factors ranging from 0.2 to 50  $\mu\text{g}$  chloroform/ mg chlorine spike. These values are not all taken from experiments completed on wastewater. Column 2 describes the media spiked to reach the formation factor shown in the third column. Some of these studies are discussed below.

**Table 2: Formation Factors found in Various Water Types**

Publication	Media Chlorinated	Average FF $\mu\text{g}/\text{mg}$
Chambon <i>et al.</i> (1983)	urine	15
Chou (1990)	raw wastewater Ammonia = 8 mg/L	0.9 – 1.9
Chou (1990)	nitrified secondary effluent Ammonia = 0 mg/L	8.0 – 12
Chou (1990)	non-nitrified secondary effluent Ammonia = 8 mg/L	0.2 – 0.4
Urano <i>et al.</i> (1983)	humic substances dissolved in water	~ 1.0 *
Peters <i>et al.</i> (1980)	humic substances dissolved in river water	~ 22
Amy <i>et al.</i> (1984)	Derived from 6 natural waters and 4 synthetic waters with low ammonia and high bromide content	26 – 51

Glaze <i>et al.</i> (1979)	buffered lake water (to pH 6.5)	7.6
Chow and Roberts (1981)	Non-nitrified activated sludge effluent	0.8 - 1.1 *
Chow and Roberts (1981)	Nitrified, extended aeration activated sludge effluent	4.8 - 7.7 *
Cooper <i>et al.</i> (1977)	Raw wastewater primarily residential spiked for 2 hours	1.8
Cooper <i>et al.</i> (1977)	Raw wastewater primarily residential spiked for 24 hours	2.1
Gurol and Itell (1989)	Aquatic fulvic acids	2.8
Van Leeuwen and Rossum (1990)	Activated sludge effluent	2.1
Dore <i>et al.</i> (1982)	Raw wastewater Low COD and Ammonia Levels	10
Dore <i>et al.</i> (1982)	Raw wastewater High COD and Ammonia Levels	1
Scully <i>et al.</i> (1984)	Humic Acids (no competing reactions)	5
Scully <i>et al.</i> (1984)	Bovine Serum Albumin (no competing reactions)	3

\* Formation factors based on total trihalomethane formation.

Chou (1990) studied chloroform formation in raw wastewater, nitrified secondary effluent and non-nitrified secondary effluent. Subsequent formation factors listed in Table 2 were calculated using the chloroform concentration in wastewater after a one hour spike period and chlorine dose concentrations of 5 and 15 mg/L. Chou (1990) reported that the presence of ammonia in wastewater had a significant impact on the formation of THMs. It was observed that even though the TOC of the nitrified and non-nitrified wastewater were approximately the same, the formation of chloroform was significantly greater in nitrified (low ammonia) wastewater. Concentrations of chloroform formed in non-nitrified effluent and raw wastewater were a factor of 10 lower than those formed in nitrified secondary effluent.

However, Chou (1990) reported chloroform formation for chlorination levels below breakpoint, and cautioned that chlorination above breakpoint would lead to significantly higher levels of THM formation once the competitive effects of ammonia were removed.

Cooper *et al.* (1977) chlorinated primarily residential raw wastewater and reported relatively high concentrations of THMs formed before breakpoint. It was stated that monochloramines do not react with aquatic organics to form THMs. However, because of the concentrations of THMs observed during chlorination before breakpoint was reached, it was hypothesized that there may be a multistep process involved in THM formation. Cooper *et al.* (1977) concluded that chloroform and brominated THMs were formed in wastewater before and after

chlorination breakpoint, and the concentration of individual THMs tended to follow the breakpoint curve (i.e. exhibited lower concentrations near breakpoint). The results, however, did not exhibit a clear trend in terms of the rate of THM formation with respect to the amount of chlorine added. The observed formation factors ( $\mu\text{g}$  chloroform formed/mg chlorine spiked ( $\text{Cl}_2$ )) for below breakpoint concentrations of chlorination ranged from 1.7 to 2.1  $\mu\text{g}/\text{mg}$  for raw (primarily residential) wastewater.

Dore *et al.* (1982) studied the effects of precursor type, pH, ammonia concentration and COD on the formation of trihalomethanes in different waters and wastewater. For the studies completed using wastewater, it was observed that the formation factors varied widely as a function of COD and ammonia concentration. For COD and ammonia levels of 300 mg/L and 68 mg/L respectively, the formation factor was approximately 1.1  $\mu\text{g}/\text{mg}$ . For COD and ammonia concentrations at 50 mg/L and 0.7 mg/L respectively, it was found that the formation factor was 11  $\mu\text{g}/\text{mg}$ .

Chow and Roberts (1981) chlorinated two different partially treated wastewaters to observe the formation of halogenated by-products. These wastewaters were effluent from an activated sludge process and effluent from an extended aeration activated sludge process (which produced a nitrified effluent). The ammonia concentrations ranged from 20–35 mg/L and <0.06 – 0.2 mg/L respectively. The wastewaters were spiked with chlorine levels of 20 mg/L and 40 mg/L and incubated for 1 hour to 24 hours. Formation factors were then

calculated using the total THM concentration formed after the 24 hour incubation period. The formation factors observed for this study ranged from approximately 1.8 to 1.1 for the activated sludge process effluent and 4.8 to 7.7 for the nitrified, extended aeration activated sludge process effluent.

Scully *et al.* (1984) chlorinated various types of proteins in buffered water to pH 7.0), without the presence of competing reactions such as COD or ammonia. Solutions of Bovine Serum Albumin (BSA) and humic acids were made up to 5 mg/L and chlorinated to 20 mg/L. It was found that the chloroform formed from the BSA solution was much slower than that from the humic acid solution at incubation times of one day. The formation factors observed over a 24 hour period were approximately 3 for BSA and 5 for humic acids.

Urano *et al.* (1983) completed studies involving the chlorination of known quantities of humic substances dissolved in water. Chlorine doses and TOC concentrations varied from 2 mg/L to 100 mg/L and 2 mg/L to 50 mg/L, respectively. The authors varied pH from 3 to 10, and studied reaction rates from initial spiking to incubation times of up to 100 hours. Their findings indicated a rapid increase in THM formation for the first few hours after chlorination, followed by a slower increase in formation thereafter. Thus, it was observed that THM formation increased linearly with TOC of humic acids, as well as with pH. This observation is not consistent with later findings of maximum THM yield at pH 8.3 for wastewater (Stenstrom *et al.*, 1987). However, THM formation in wastewater is complicated by the effects of pH on ammonia chemistry and subsequent chlorine

scavenging efficiency. Finally, Urano *et al.* observed THM formation factors of approximately 1 µg/mg of Cl<sub>2</sub> addition. They provided the following empirical expression:

$$C_{THM} = 3.5 \times 10^3 \exp^{-4.47 \times 10^3 / T} (pH - 2.8) C_{TOC} C_{Cl_2_0}^{.25} t^{.36} \quad (8)$$

where  $C_{THM}$  is the concentration of trihalomethanes in mg/L,  $T$  is temperature in °C,  $C_{TOC}$  is the concentration of humic acids in mg/L,  $C_{Cl_2_0}$  is the initial dose of chlorine in mg/L and  $t$  is time in hours.

Peters *et al.* (1980) studied the formation of chloroform in river water spiked with chlorine at 8 mg/L. Water temperature was maintained at 10°C, and initial humic acid concentration was 5 mg/L. Reaction rates for chloroform formation during an incubation period of 0 days to 24 days were also studied. It was observed that chloroform formation in the presence of humic and fulvic acids took place in two phases. The first phase was very rapid and highly pH dependent. The second phase was slower and less dependent on pH. A linear relationship between chlorine consumption and chloroform production was reported. However, chloroform formation only accounted for a small portion of total chlorine consumed. Based on their experimental data, Peters *et al.* (1980) reported the following relationship for chloroform formation (neglecting the effects of pH and ammonia concentration):

$$C_t = 0.022 [(Cl_2)_0 - (Cl_2)_t] \quad (9)$$

where  $C_t$  is chloroform concentration in mg/L at time  $t$ ,  $(Cl_2)_0$  is initial chlorine

concentration in mg/L and  $(\text{Cl}_2)_t$  is chlorine concentration at time  $t$  in mg/L. For complete consumption of chlorine, Equation 9 predicts approximately 22 times the THM yield (assuming the majority of THM is chloroform) observed by Urano *et al.* (1983).

Van Leeuwan and Rossum (1990) studied the formation of trihalomethanes during chlorination to reduce bulking in activated sludge systems. The main THM formed was chloroform and formation factors were observed in the range of 4  $\mu\text{g}/\text{mg}$  of  $\text{Cl}_2$  spike. This formation factor was fairly consistent up to chlorine spike levels of 100 mg/L. Higher spike levels did not increase the mass of chloroform formed, which appeared to reach a maximum regardless of the increase in chlorine spike level.

A summary of formation factors found in various studies is provided in Table 2. Of particular interest are the formation factors observed by Chou (1990), Cooper *et al.* (1977) and Dore *et al.* (1982). These sets of experiments were completed by spiking raw wastewater, and resulted in formation factors ranging from 0.9 to 2.1  $\mu\text{g}/\text{mg}$ .

### **3.0 EXPERIMENTAL METHODOLOGY**

Raw wastewater samples were spiked with a 12 % sodium hypochlorite solution and analyzed using gas chromatography with mass selective detection (mass spectrometer) to determine the quantity of chloroform formed as a function of chlorine dose in wastewater. Wastewater was characterized by the following parameters: total organic carbon, ammonia, suspended solids and pH. Formation factors were determined to relate sodium hypochlorite spike levels to levels of chloroform formed.

The remainder of this chapter provides detailed descriptions of laboratory experiments, as well as sample analytical methodologies for chloroform formation and each of the aforementioned wastewater parameters.

#### **3.1 TRIHALOMETHANE FORMATION EXPERIMENTS**

Seventeen sets of wastewater samples were tested for chloroform formation using 12% sodium hypochlorite spike solutions. Initial wastewater sets (1 to 6) were spiked from 0 (no spike) to 200 mg/L to examine high end chloroform formation. The final 10 wastewater sets (8 to 17) were spiked at chlorine concentrations of 0 to 100 mg/L with a focus on lower spike levels ( <50 mg/L). One sample set (set 7) was completed for spike levels of 0 to 30 mg/L to examine linearity of formation at low end spike concentrations. A summary of sampling events and corresponding chlorine spike levels is provided in Table 3.



### 3.1.1 SAMPLE COLLECTION

Raw wastewater was collected from a channel connecting mechanical bar screens to grit removal chambers at the Guelph Wastewater Treatment Facility. The City of Guelph Wastewater Treatment Facility services approximately 80% residential and 20% commercial/industrial wastewater.

An access hole allowed samples to be collected directly from the wastewater stream before aeration in the grit chambers. This minimized loss of pre-existing chloroform present in the raw wastewater.

Because samples were collected at the very end of the sewer system, previous exposure of wastewater samples to chlorine could not be avoided. This previous contact of wastewater with chlorine would cause loss of some precursors to THM formation as well as loss of some competing parameters (e.g. ammonia and metals) to reactions with chlorine. The overall effects of these changes were not studied. However, based on the probable high levels of both organic precursors and competing compounds (ammonia and other inorganics) present in untreated municipal wastewater, the effects of upstream chlorination should not have been significant. To ensure consistency in pre-exposure to chlorine, the samples were all collected at the headworks of the treatment facility.

Samples were collected in 1.0 L glass bottles with Teflon lined plastic caps and transported directly to the Environmental Engineering laboratory at the University of Guelph. Wastewater characterization (pH and concentrations of TOC, ammonia and solids) and chloroform formation factor experiments were completed

on the same day the sample was collected.

### **3.1.2 PREPARATION OF WASTEWATER SAMPLES**

In preparation for chlorine spiking, 40 mL glass vials, with screw caps with holes in the centre containing polytetrafluoroethylene (PTFE) lined silicone septa, were cleaned using phosphate-free detergent, rinsed with distilled, deionized water and baked at 100°C for a one hour period in a Baxter temperature-controlled oven to ensure the absence of organic contaminants. Vials were filled (using a 50 mL graduated cylinder cleaned as described above) to capacity with wastewater to avoid a headspace. Preliminary and duplicate vials were filled with wastewater for each chlorine spike level (2 vials for each spike level). For each experiment, two vials were also prepared to determine chloroform concentrations in raw wastewater (i.e., 0 mg/L chlorine spike).

### **3.1.3 CHLORINATION AND REACTION**

Sodium hypochlorite (labelled 12% by mass) was obtained from KERT® Chemical Industries. Chlorine analyses of the sodium hypochlorite solution were completed by the DPD (diethyl-p-phenylene diamine) ferrous titrimetric method (see section 3.4 for methodology) in order to confirm chlorine levels in the stock bleach solution. Chlorine was determined to be at 30 mg/mL during preliminary analyses (September, 1991) and 27 mg/mL during final analyses (April, 1992). The 30 mg/mL as  $\text{Cl}_2$  is equivalent to 3% by mass as  $\text{Cl}_2$  or 12% by mass as

NaOCl. Therefore, little deterioration of the stock bleach solution occurred over the eight month period of analyses.

Preliminary formation studies were completed with spike levels ranging from 0 to 200 mg/L  $\text{Cl}_2$ . These spike levels were observed to be below breakpoint. It is estimated that a molar ratio of 3:2 chlorine to ammonia is necessary to reach breakpoint in waters containing ammonia (Snoeyink and Jenkins, 1980). This is equivalent to a mass ratio of approximately 7:1 chlorine to ammonia, and does not account for the additional chlorine needed to overcome demands by non-ammonia inorganic and organic compounds. The average ammonia concentration for wastewater used in this study was 28 mg/L. Thus, a minimum of 200 mg/L of chlorine would be needed to reach breakpoint for the wastewater used in this study.

Injections of stock bleach solution were completed using 10 or 100  $\mu\text{L}$  glass syringes to reach desired concentrations of chlorine in vials containing wastewater. Chlorine doses led to chlorine concentrations ranging from 0 to 200 mg/L (Table 3) shows sampling event and chlorine spike levels). Spike levels were varied over the different sampling events as time constraints controlled the number of spike levels that could be examined in one sampling event. For the first 6 sampling events, high level spike concentrations were used in order to identify all of the chlorinated compounds formed following chlorination. Only chloroform was formed in any detectable amount. Therefore, for the all of the subsequent sampling events, it was the only compound that was studied.

All vials, including those containing raw wastewater (no spike), were shaken at room temperature using a Labline multi-wrist action shaker, for an incubation period of two hours. Vials were then stored at 4 °C until GC/MS analyses were completed (within 48 hours).

**Table 3: Sampling Event and Chlorine Spike Levels**

Sampling Event	Date	Chlorine Spike Levels (mg/L Cl <sub>2</sub> )
1	Sept 16, 1991	0,15,30,100
2	Sept 30	0,50,100,200
3	Oct 1	0,50,100,200
4	Oct 5	0,50,200
5	Oct 7	0,50,200
6	Oct 9	0,50,200
7	Nov 1	0,5,10,30
8	Nov 13	0,2,5,10,50,100
9	Dec 8	0,2,5,10,50,100
10	Dec 11	0,2,5,10,50,100
11	Dec 15	0,2,5,10,50,100
12	Jan 18, 1992	0,5,10,50
13	Jan 22	0,5,10,50
14	March 23	0,2,5,10,50,100
15	March 26	0,2,5,10,50,100
16	April 24	0,2,5,10,50,100
17	April 25	0,2,5,10,50,100

Residual chlorine analysis was completed on the spiked samples after the incubation period to verify that reactions were complete. Minimal amounts of combined and free residual chlorine were observed. Therefore, the reactions were assumed to be complete.

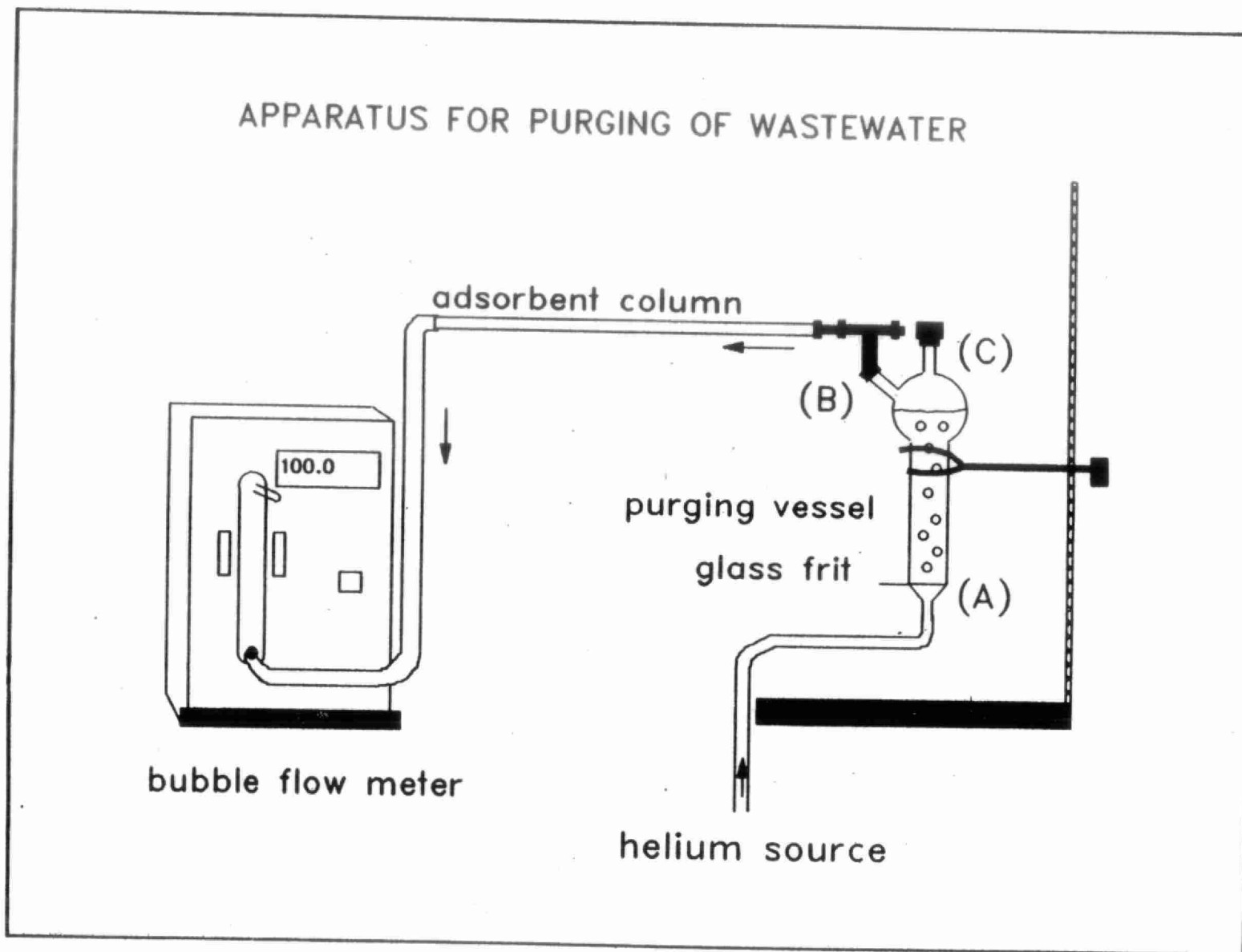
#### **3.1.4 PRECONCENTRATION OF CHLORINATION BYPRODUCTS**

Following incubation, 5 to 10 mL samples were drawn out of each vial with a 10 mL glass syringe and transferred to a 20 mL purging vessel so that volatile compounds could be purged onto a concentrating adsorbent column. The transfer syringe and the purging vessel were cleaned between each sampling with two washes of Millipore-filtered water.

The purging apparatus is shown in Figure 4. It consisted of an inlet port (A) at the bottom of the purging vessel for nitrogen or helium input and two outlet ports (B and C) at the top for effluent nitrogen or helium exhaust. One outlet port (B) was connected, using 1/4 inch stainless steel Swagelok fittings and Teflon ferrules, to an adsorbent column. The second outlet port (C) was used to inject wastewater samples into the vessel and was sealed with a 1/4 inch stainless steel Swagelok plug during purging. Nitrogen or helium purge gas was sparged through the wastewater sample at a rate of 100 mL/min for 10 minutes. Gas flow rates were measured at the outlet of the adsorbent column using a Hewlett-Packard digital bubble flow calibrator.

Two sets of studies were completed and are hereafter referred to as

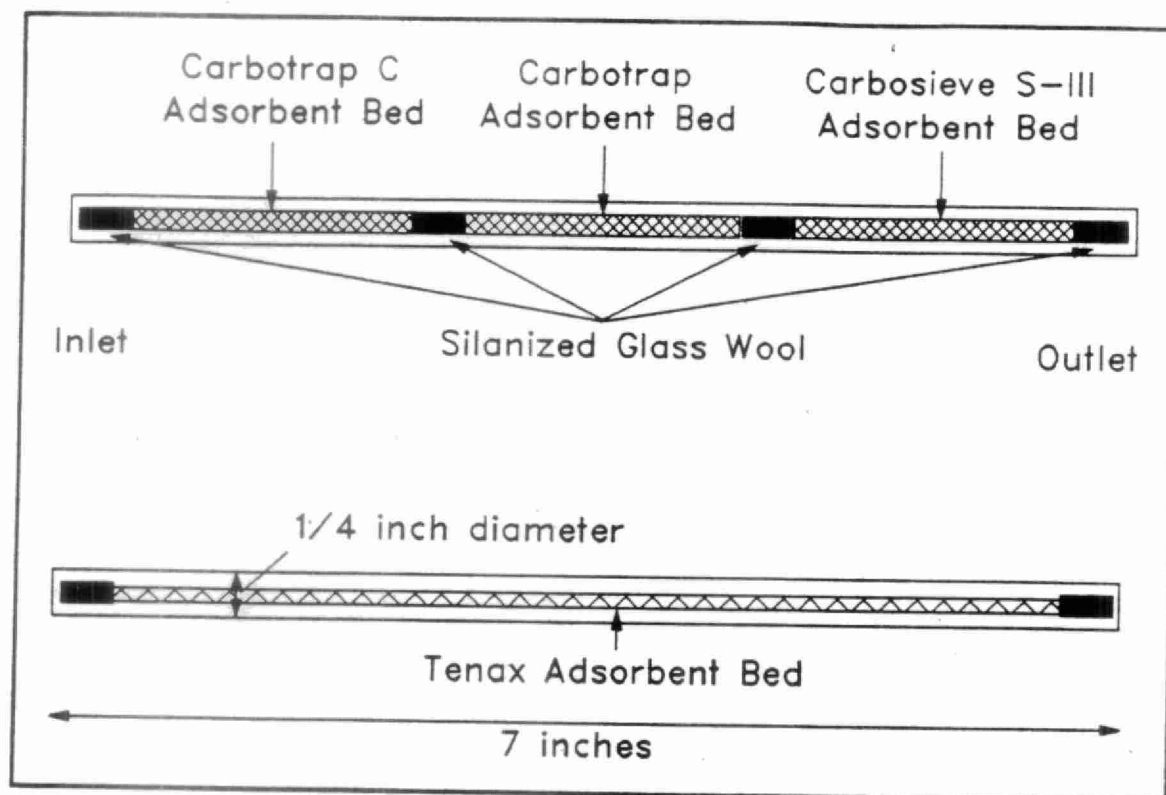
Figure 4 Apparatus for Purging of Wastewater Samples



preliminary and final experiments. During preliminary experiments, nitrogen was used as the purge gas. During these analyses, it was observed that there was minor contamination (in the form of low molecular weight hydrocarbons) of the samples that was arising from the nitrogen tank. Thereafter, high purity helium was substituted for nitrogen before final analyses were completed and an SGE Inc. gas purifier was installed upstream of the purging vessel.

Customized Carbotrap® 300 Multi-bed Thermal Desorption Tubes were used for preliminary experiments (Figure 5). These columns had a 1/4 inch outside diameter with casings of stainless steel. The inner walls were glass lined and the tubes were packed with three different materials, each separated by silanized glass wool. Packing materials included Carbotrap C graphitized carbon black, Carbotrap graphitized carbon black and Carbosieve S-III carbon molecular sieve.

During preliminary experiments, some calibration curves were characterized by relatively high y-intercepts (see Appendix B). This posed difficulties in accurately quantifying chloroform concentrations at low spike levels. Thus, Tenax (mesh 6080) was used to complete experiments 10 through 17.



**Figure 5**     **Adsorbent Columns**



### **3.2 IDENTIFICATION AND QUANTIFICATION OF THMs**

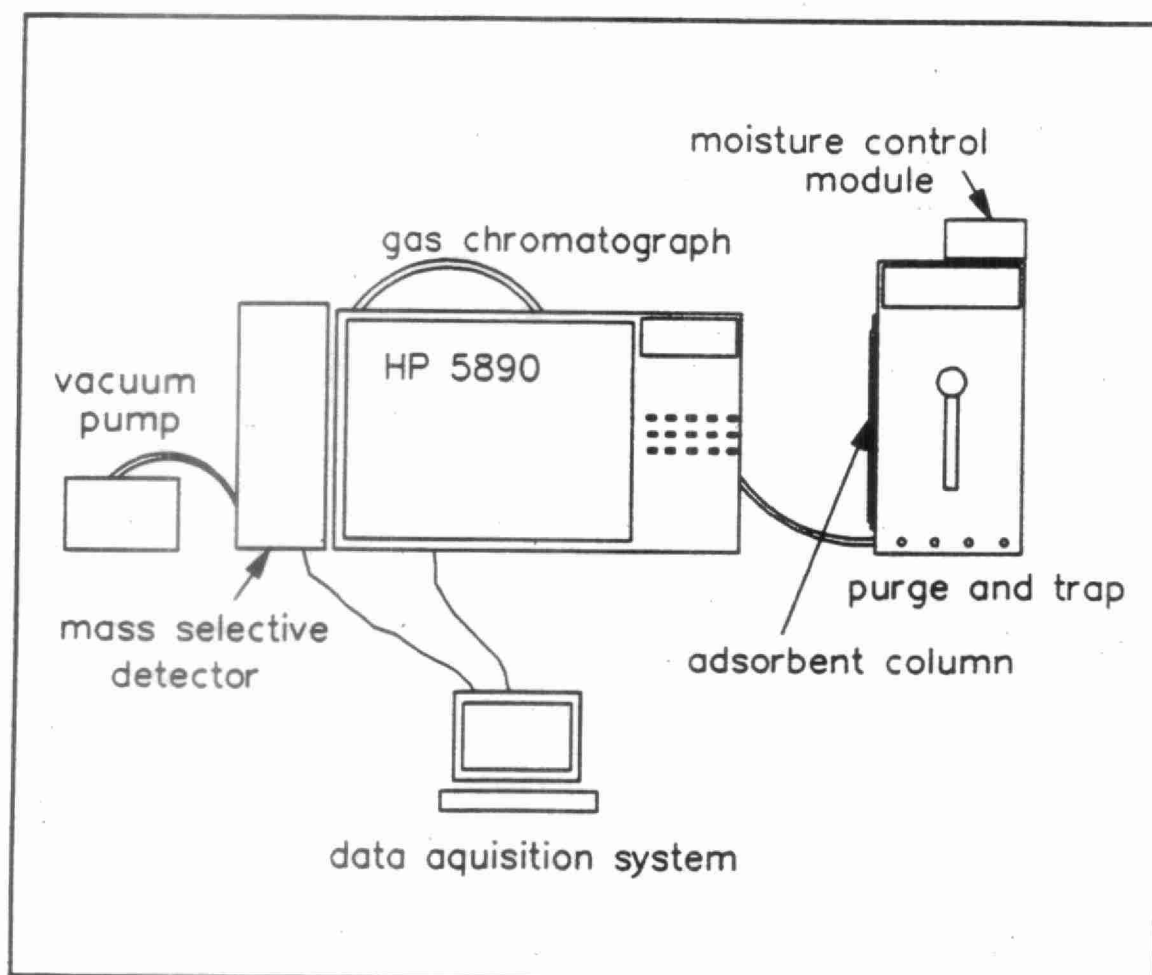
Volatile compounds sorbed to the adsorbent columns were desorbed using a purge and trap unit, separated with a gas chromatograph, and detected using a mass spectrometer. Final identification of chloroform was completed by matching retention times and mass spectra of peaks to those of a standard VOC mix.

#### **3.2.1 Thermal Desorption Followed by GC/MSD**

The contents of individual adsorbent tubes were analyzed using a Tekmar model LSC 2000 purge and trap system. The internal trap on the purge and trap unit was replaced with the adsorbent tube to allow desorption. This system was connected to a Hewlett-Packard model 5890 series II gas chromatograph equipped with a J and W Scientific 30 m narrow-bore capillary column (0.02 mm internal diameter with 1  $\mu$ m film thickness, model number 122-5033). The stationary phase was a siloxane polymer which consisted of 5% phenyl and 95% methyl. This means that there was a phenyl ring bound to 5% of the backbone silicon atoms and the remaining 95% of the silicon atoms had methyl groups bound to them. A Hewlett-Packard model 5971A mass spectrometer was used for compound identification and quantification (see Figure 6).

A full-scan (SCAN) acquisition mode was used for preliminary experiments to observe all compounds potentially formed following chlorination of the wastewater. This mode detected all compounds that passed through the gas

chromatograph. An initial temperature of 24°C in the GC oven was used as no cryofocussing unit was available. Temperature was increased at a rate of



**Figure 6:** Purge and Trap Unit with Gas Chromatography with Mass Selective Detection Setup

40°C/min to 42°C, and then at a rate of 9°C/min to 200°C. For the final experiments, Selective Ion Monitoring (SIM) acquisition mode was used to observe only the four trihalomethanes of interest to this study. An initial temperature of 24°C was again used. Temperature was increased at a rate of 40°C/min to 42°C, followed by a rate of 9°C/min to 130°C, and finally at a rate of 40°C/min to 200°C. The actual programming used for GC/MS analyses (SCAN and SIM modes) are documented in Appendix A.

Adsorbent tubes were desorbed to the GC column using the aforementioned purge and trap system. The purge and trap program consisted of a dry purge of 3.5 minutes to remove excess water. Tubes were then desorbed for 2.0 minutes for preliminary studies and 2.75 minutes for final analyses at 205°C (see section 4.1). Finally, the tubes were baked at 225°C for 2.0 minutes to remove any residual compounds.

The purge and trap system was optimized for desorb time prior to preliminary studies and then again prior to final analyses. The results of these studies can be found in Section 3.8.

### **3.2.2 Preparation of Standard Volatile Organic Compound Mixes**

Three to five point calibration curves were constructed using Supelco® standard VOC mixes 7 and 8 which collectively contained 18 volatile organic compounds (ethylbenzene, o-xylene, p-xylene, benzene, toluene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,4-dichlorobenzene, 1,1-dichloroethylene,

bromoform, bromodichloromethane, dibromochloromethane, trichloroethylene, vinyl chloride, carbon tetrachloride, chloroform, benzene) in methanol. Standard mixes were packaged in 1.0 mL glass ampules with all VOC concentrations at 2000 mg/L. Ampules were broken and their contents transferred with a 1000  $\mu$ L gas tight syringe to a 2 mL glass vials with a screw caps and Teflon-lined silicone septum. Glass vials were labelled, and volumes of methanol were added to achieve a final volume of 1.0 mL. Volumes of methanol and VOC mixes used to prepare calibration standards are listed in Table 4. Standards were mixed to allow for all calibration analyses to be based on 5  $\mu$ L standard solution volumes injected into the previously described purging vessel. In other words, five standards were made (1, 5, 20, 100, 200 mg/L mixes). This allowed for 5  $\mu$ L volumes to be taken from each of the 5 standards, and five point calibration curves in the range of 5 ng to 1000 ng (5  $\mu$ L of the 1 mg/L VOC standard is 5 ng).

**Table 4 Volumes of Volatile Organic Compound Mix and Methanol used for Calibration Standards.**

Concentration	Mass in 5 $\mu$ L of Solution	Volume of Standard	Volume of Methanol
1 mg/L	5 ng	200 $\mu$ L of 5 mg/L mix	800 $\mu$ L
5 mg/L	25 ng	2.5 $\mu$ L mix 7,8	995 $\mu$ L
20 mg/L	100 ng	10 $\mu$ L mix 7,8	980 $\mu$ L
100 mg/L	500 ng	50 $\mu$ L mix 7,8	900 $\mu$ L
200 mg/L	1000 ng	100 $\mu$ L mix 7,8	800 $\mu$ L

Volumes of methanol were measured with a 1000  $\mu$ L gas tight glass

syringe. The volumes of standard mix were measured as follows:

2.5  $\mu\text{L}$  – 5  $\mu\text{L}$  glass syringe

10  $\mu\text{L}$  – 10  $\mu\text{L}$  glass syringe

50  $\mu\text{L}$  – 100  $\mu\text{L}$  glass syringe

100  $\mu\text{L}$  – 100  $\mu\text{L}$  glass syringe

200  $\mu\text{L}$  – 250  $\mu\text{L}$  glass syringe

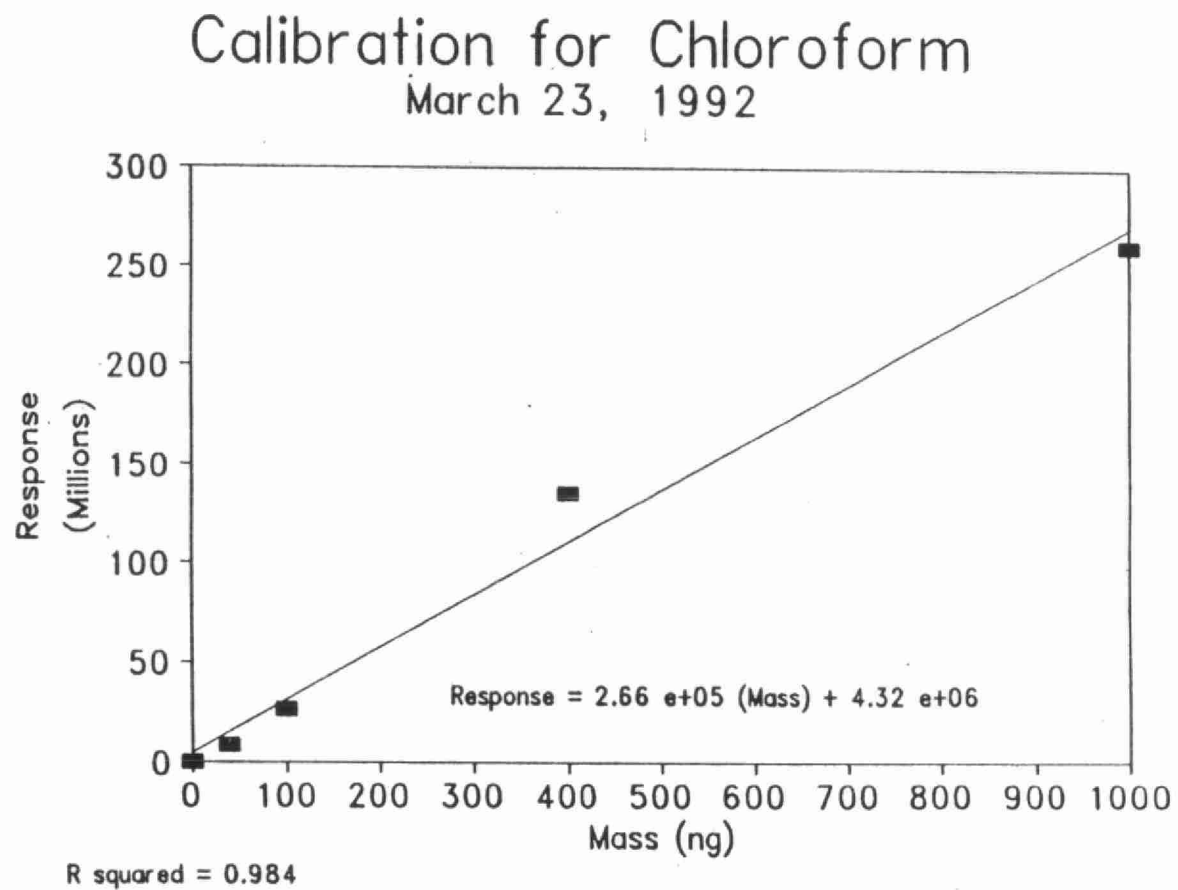
A second 20 mL sparging vessel (separate from the one used to purge chlorinated wastewater samples) was used to purge standards from distilled water which had been prepurged with helium to ensure the absence of THMs. The purging vessel had a separate arm in the mid section with a septum to allow for standard volumes to be directly injected into the vessel. Five microlitre volumes of standard VOC mix were injected and purged with nitrogen at 100 mL/min for 10 minutes. The aforementioned procedure described for quantification of VOCs in spiked wastewater was also followed for analysis of calibration standards and calibration curves were constructed for mass ranges to be examined in the spiked samples (see section 3.2.1).

### **3.2.3 Construction of Calibration Curves**

The mass spectrometer could function up to a loading of 2 to 3  $\mu\text{g}$  of any given compound before the vacuum in the detector was broken. Therefore, calibration curves were completed from 5 ng to 1  $\mu\text{g}$ , and spiked wastewater sample volumes were selected so that less than 1  $\mu\text{g}$  of chloroform was loaded

onto the detector for any given sample. Prior to construction of each calibration curve, a system blank was prepared by purging 10 mL of distilled, deionized water for 10 minutes in a procedure identical to that used for purging of standards. The response observed from this "blank" was used as a fourth or fifth point on all calibration curves. A sample calibration curve is provided in Figure 7 based on sample analyses completed on March 23, 1992. All other calibration curves are provided in Appendix B. The calibration curves had an average R-squared value of 0.971 and a range of 0.879 to 0.996.

Figure 7 Sample Calibration Curve



### 3.3 AMMONIA ANALYSIS

Wastewater samples collected from the Guelph Wastewater Treatment Facility were analyzed for ammonia concentrations within 24 hours of collection. The wastewater samples were stored at 4°C before analysis.

Ammonia analyses were completed, according to Standard Methods, by the phenate titration method (Standard Methods, 1989). This method involved a preliminary distillation step to eliminate interferences caused by cyanates and organic nitrogen found in wastewater. An illustration of the apparatus used for the preliminary distillation is provided in Figure 8. Specific details of ammonia analyses are listed in Standard Methods, with a methodology summary provided in Appendix D and results in table 9. Distillation was performed by bringing the pH of wastewater samples above 9.5 and boiling. The distillate was collected into an indicating boric acid receiving solution (pH 2) at a rate of approximately 6 mL/min until at least 250 mL of distillate had been collected. This solution was then titrated (using a 50 mL graduated burette) from a green to purple end point with a 0.02 N sulfuric acid solution. The phenate titration method was considered to be the most efficient for ammonia analysis as the distillation stage eliminated most interferences (alkalinity over 500 mg as calcium carbonate, acidity over 100 mg as calcium carbonate and turbidity) found in the wastewater.

During all preliminary experiments (experiments 1 through 7), ammonia analyses were completed in duplicate. An analysis blank was also run using the same procedure and distilled deionized water in replace of wastewater. This step



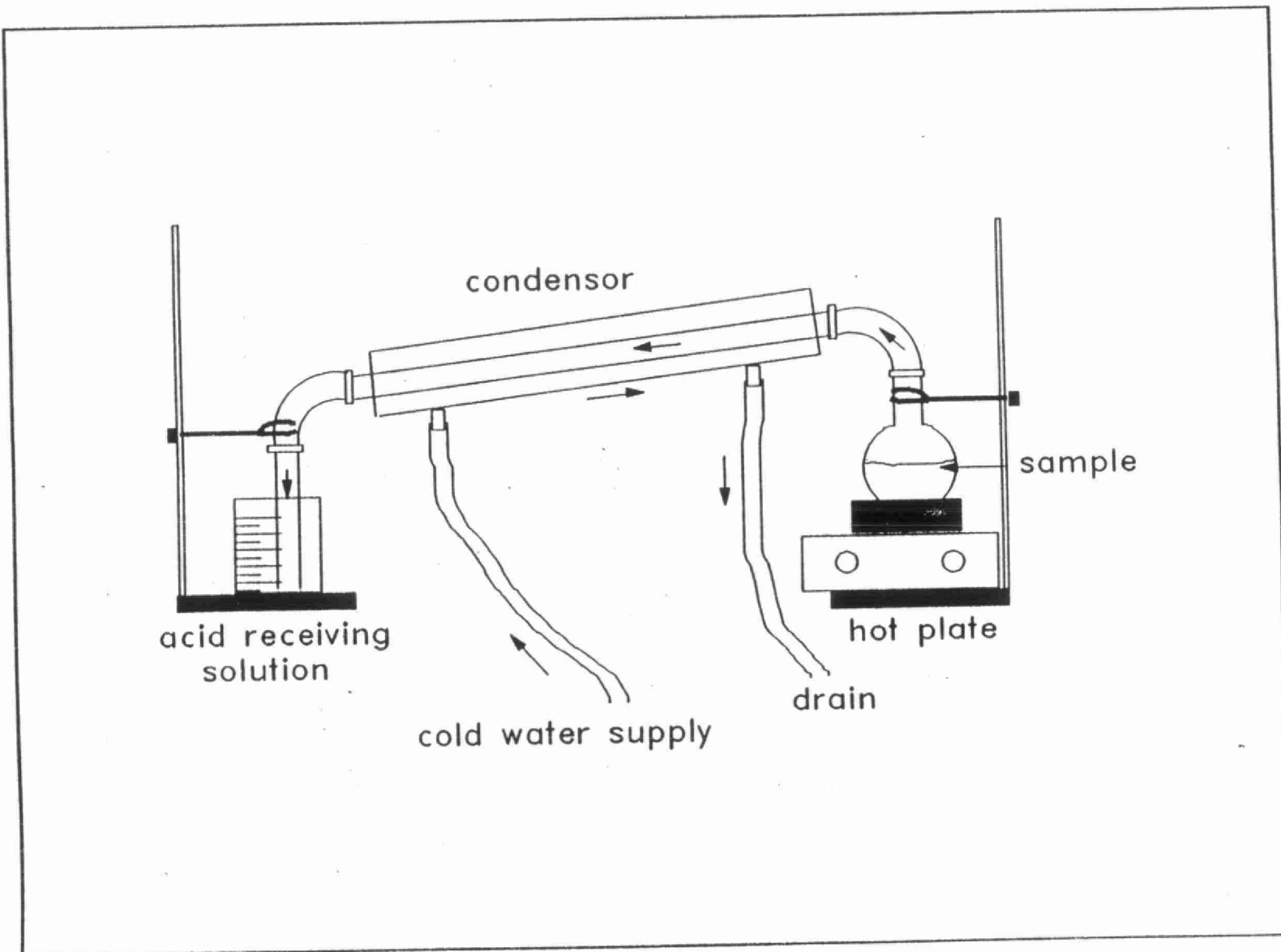


Figure 8 Apparatus for Preliminary Distillation of Ammonia

ensured no interferences from contaminated glassware or solutions used in the preliminary distillation stage. During all experiments, ammonia concentrations of raw wastewater always exceeded 18 mg/L. Furthermore, it was observed that duplicates varied in concentration from only 0.1 mg/L to 0.5 mg/L. The method was considered to be precise to 1.0 mg/L ammonia. Therefore, duplicates were not completed after this observation.

### 3.4 CHLORINE ANALYSIS

The DPD (N,N-diethyl-p-phenylenediamine) ferrous titrimetric method was used for chlorine analysis according to Standard Methods (Standard Methods, 1989). This method is the least affected by oxidized forms of manganese common in wastewater. The DPD method was also capable of differentiating between free and combined chlorine as well as between mono-, di- and trichloramines if necessary.

Bromine and iodine ions present in the spiked wastewater solution can interfere with the DPD ferrous titrimetric method. However, the competing reactions of other halogen ions were not considered important as their concentration in comparison to residual chlorine in the spiked samples was assumed to be negligible. The sodium hypochlorite solution used for this study was labelled at 99% pure. Therefore any other halogens present in the solution are assumed to be less than 1% (by mass) of chlorine.

The DPD method uses ferrous ammonium sulfate (FAS) to titrate samples

to which a commercially available DPD indicator has been added in tablet form. Total residual chlorine was determined by direct titration with FAS solution (from a 25 mL graduated burette) until all red colour disappeared. It was expected that for chlorination below breakpoint there would be minimal free residual chlorine present. This was observed during preliminary experiments when wastewater samples were analyzed for free residual chlorine before and after spiking.

Chlorine analyses were also completed on the sodium hypochlorite stock bleach solution during preliminary studies and again prior to final analyses to ensure that no degradation of the spike solution had occurred. Initially, the stock bleach solution was observed to have a concentration of 30 mg/mL  $\text{Cl}_2$ . At the conclusion of all experiments, it had a concentration of 27 mg/mL  $\text{Cl}_2$ . Based on these results, it was assumed that no significant degradation of the sodium hypochlorite stock bleach solution had occurred over the course of the seventeen formation experiments.

The standard FAS solution was prepared in a 1.0 L volumetric flask. A mass of 1.106 g of FAS was added to distilled water containing 1 mL of 1 part  $\text{H}_2\text{SO}_4$  to 3 parts water and made up to 1.0 L. This solution was prepared monthly and stored in a tinted glass reagent bottle. Chlorine content was calculated as  $\text{FAS} = 100 \mu\text{g Cl}/1.00 \text{ mL}$  and checked by titrating standard chlorine water.

### 3.5 TOTAL ORGANIC CARBON ANALYSIS

Total organic carbon (TOC) concentrations in raw wastewater samples were

quantified at the Land Resource Science analytical laboratory at the University of Guelph. A Technicon auto analyzer using colorimetric determination was used to complete these analyses.

The Technicon auto analyzer had previously been used solely for solid samples (in particular for TOC analysis in soils). Unfortunately, the staff at Land Resource Science did not filter the samples which were dried in an oven at 100°C. The residual was used to quantify TOC. This procedure created two probable errors in the results. First, TOC results included all organic material; not only that dissolved in the water but also in the form of suspended organic material. Second, drying the samples at 100°C likely volatilized some dissolved organic material in the samples before TOC analyses could be completed.

Total organic carbon analyses completed on the wastewater samples are reported in Section 5.0. However, the uncertainties associated with TOC measurements prohibited their direct use in this study. Subsequent analyses of TOC in untreated Guelph wastewater have been completed by a commercial laboratory. These samples suggest typical TOC (dissolved) concentrations of 50–60 mg/L.

### **3.6 SOLIDS ANALYSIS**

Total and volatile suspended solids analyses were completed according to Standard Methods (Standard Methods, 1989). Wastewater samples with volumes in the range of 50 mL to 100 mL were filtered using Whatman® glass microfibre

filters (4.7 cm, 934-AH) and a vacuum filtration unit. Filter papers were predried at 100°C, cooled in a desiccator and weighed on a precision balance (mass 1). After filtration, filter papers were dried again at 100°C for one hour, cooled and weighed (mass 2). Filter papers were then placed in a muffle furnace for 20 minutes at 515°C, cooled in a desiccator and weighed (mass 3). Total suspended solids concentrations were calculated as follows:

$$(\text{TSS}) = (\text{mass } 2 - \text{mass } 1)/\text{volume filtered}$$

Volatile suspended solids concentrations were calculated as follows:

$$(\text{VSS}) = (\text{mass } 2 - \text{mass } 3)/\text{volume filtered}$$

All wastewater samples were analyzed for TSS and VSS within 24 hours of collection and stored at 4°C until analysis was completed.

Using a 100 mL graduated cylinder, 100 mL of wastewater was measured. A wastewater volume of 50 mL was poured from the graduated cylinder to the vacuum filtration unit and the length of time required for the sample to be filtered was noted. If the 50 mL of wastewater travelled directly through the filter paper, the full 100 mL of wastewater sample was filtered and this volume was used to calculate TSS and VSS. If the 50 mL sample required a significant amount of time to pass through the filter paper (e.g. more than one minute), only the 50 mL sample was used for determination of TSS and VSS. This procedure was used as it ensured that a sufficient mass of solids was trapped on the filter paper to reduce error in results, and to ensure that the filter paper was not overloaded with solid material. If too much solid material was trapped on the filter paper,

particulate matter that would normally have passed through the paper would have been trapped, giving results which overestimated TSS and VSS concentrations.

All samples for TSS and VSS were run in duplicate and the results averaged from the two values obtained. Duplicates for TSS analyses varied from 1% to 40% with an average of 15%, and duplicates for VSS varied from 2% to 44% with an average of 15%. Variations as high as 44 percent can be accounted for by the fact that wastewater samples are not homogenous and one or more particles of significant mass can cause variations in solids analysis in this range.

### **3.7 Quality Assurance**

"Quality assurance is defined as a planned system of activities whose purpose is to provide assurance that a quality control program is actually effective" (Garfield, 1984).

#### **3.7.1 Laboratory Analysis**

Various measures were taken to ensure the quality of experiments and sample analyses. These included an investigation of the effects of wastewater age, chloroform concentrations in stock bleach solution, performance of adsorbent columns and purge and trap unit, and maintenance of the GC/MS.

#### **Effects of Wastewater Age**

A study was completed to examine the difference in chloroform formation

of wastewater that was spiked directly after collection and 24 hours after collection. Initial analyses showed that no residual chlorine was present in the raw wastewater samples. However, due to the highly varying characteristics of the wastewater, analyses were always completed to verify this assumption.

Wastewater was collected on September 30, 1993 and separated into two aliquots. One portion was analyzed for chloroform formation (as described in Section 3.0) within two hours of collection. The second portion was kept at 4°C for 24 hours and a subsequent formation study was completed. Results of these studies are shown in Figure 9.

At spike levels of 100 and 200 mg/L, the ratios of chloroform formed in aged to chloroform formed in "fresh" wastewater were 0.6 and 0.6, respectively. These results suggest that variations in formation factors may be obtained if the wastewater is allowed to age (although no statistically conclusive results could be obtained from this data set). No studies were completed to assess the reason(s) for the difference in formation of chloroform in aged to "fresh" wastewater i.e. wastewater characterization. All formation studies were initiated within two hours of wastewater collection to alleviate any problems potentially caused by wastewater aging.

#### **Gas Chromatograph with Mass Selective Detection Performance Criteria**

A number of different mass spectrometer responses were monitored. The compound used as the predominant measure of mass spectrometer performance

CHLOROFORM FORMATION  
VARIATIONS DUE TO AGE OF WASTEWATER

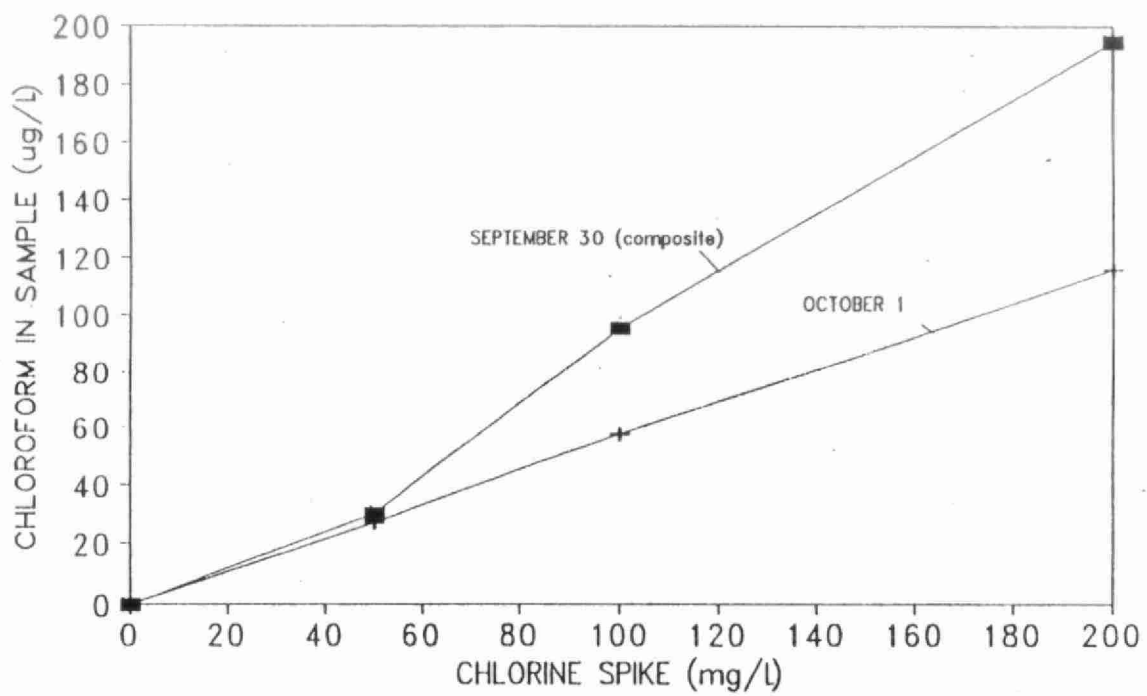


Figure 9 Variation in Formation with Age of Wastewater



was perfluorotributylamine,  $[(C_4F_9)_3N]$ , PFTBA). This compound is stable, i.e. not thermolabile, and was therefore selected by the instrument manufacturer as a compound to test mass spectrometer performance. The PFTBA fragments range in mass from low to high. Chloroform has a mass which falls comfortably between the mass range of PFTBA fragments.

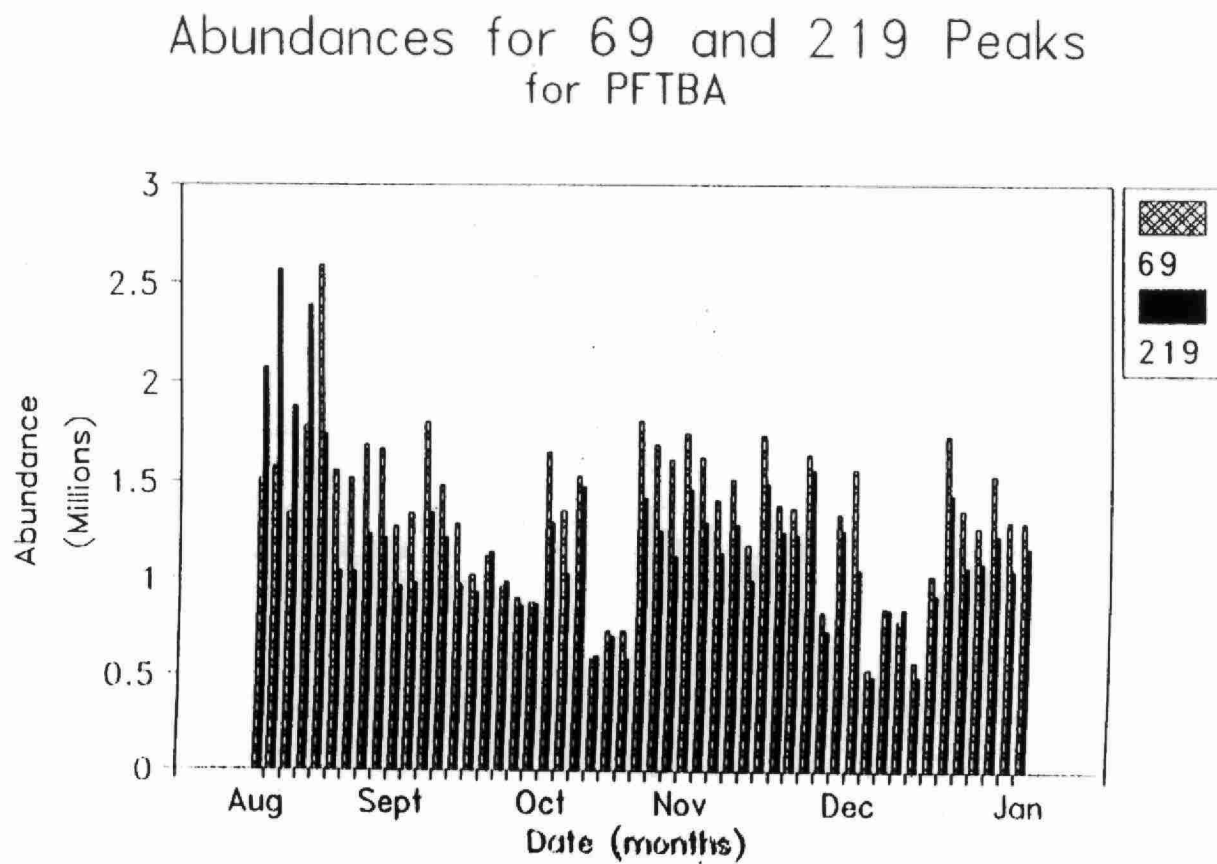
Figure 10 shows the response of the mass spectrometer to peaks 69 and 219 of PFTBA over time (August to October). The net decrease in response over time was believed to be caused by a number of factors, including the build-up of non-volatile material on the detector.

When the responses (abundances) of ions 69 and 219 peaks were low (below 1,000,000), the system was baked for an extended period of time (up to 12 hours), in order to clean the system. The system was tuned if baking was not successful. This procedure was repeated until the response of ion 69 exceeded 1,000,000.

If variations in the PFTBA ion 69 response were greater than 20% from day to day, analyses were not completed. Baking of the system or a re-tune were completed until variations in the response were less than 20%.

Monitoring was also completed during run time periods. Calibration curves were completed at the start of run periods. Midpoint calibration standards were run after 10 to 15 samples had been analyzed and again at the end of the run period. This ensured that response of the mass spectrometer did not vary over the course of analysis. If the difference in response to the midpoint calibration

Figure 10 Perfluorotributylamine Monitoring



standards before and after samples were run was greater than 20%, the samples were not considered valid. Investigation into the cause of the varying response was then completed.

### **Determination of Chloroform in Stock Bleach Solution**

Due to the very high concentration of chlorine in the stock bleach solution, it was thought that concentrations of chloroform in the bleach could interfere with spiked samples (i.e., introducing chloroform to samples directly and without reaction). Experiments were therefore completed to determine the concentration of chloroform in the sodium hypochlorite stock bleach solution.

Four of seven vials were prepared using 40 mL of Millipore filtered water, 0.6 to 6 mg of sodium sulfite, and concentrations of 5 and 50 mg/L sodium hypochlorite in 40 mL glass vials (with screw caps and Teflon septa). Sodium hypochlorite was then injected into the remaining 3 vials to yield chlorine concentrations of 5, 10 and 50 mg/L. Each of these samples was then analyzed using the GC/MS to determine chloroform concentrations (see laboratory analysis section for procedures). Resulting chloroform concentrations are shown in Table 5.

The concentration of chloroform in spiked wastewater is reported in Table 5 with the concentration of chloroform in the spiked water directly below. Although lower than chloroform concentrations in wastewater spiked with equivalent amounts of chlorine, relatively high concentrations of chloroform were observed

in the spiked distilled water samples. Concentrations of chloroform observed in the spiked distilled water were approximately 25% to 50% of those observed in the spiked municipal wastewater.

Chloroform observed in spiked distilled water could have arisen from:

1. reaction of chlorine with residual organics in the water or on the glass vials,
2. reaction of hypochlorite gas with the packing material of the adsorbent columns,
3. chloroform pre-existing in the sodium hypochlorite solution.

Further analyses were completed to determine the source of chloroform in the spiked distilled water samples.

Glass vials (40 mL with screw caps and Teflon septa) were washed with phosphate free detergent, rinsed with distilled deionized water and baked at 550°C for 20 minutes. This ensured that no residual organics remained on the vial walls. Vials were cooled in a desiccator and filled with Millipore filtered water. Chlorine spike levels of 5 and 50 mg/L were used to assess the origin of the chloroform found in the previous spike distilled water samples.

To ensure that the sodium hypochlorite solution was totally reacted, sodium sulfite was added to the Millipore filtered water prior to spiking. Molar ratios of 3:1 were used (sodium sulfite : chlorine). By adding sodium sulfite, the possibility of chloroform forming on the adsorbent columns or chlorine reacting with residual organics in the vial could be ruled out, i.e. if chloroform was observed it would be due to chloroform already present in the sodium hypochlorite solution.

Table 5 shows the results of spiked distilled water with and without the use of the sodium sulfite. Chloroform levels were consistently below the detection limit (approximately 1  $\mu\text{g/L}$  depending on the sampling event) in the solution containing sodium hypochlorite. This implies that no error in formation factor calculations occurred from chloroform already existing in the spike solution. However, chloroform formed in distilled water solutions not containing sodium sulfite must have arisen from reaction on the adsorbent columns or reaction with residual organics on the vials or in the distilled water.

For formation experiments using wastewater, there was little chance that gaseous chlorine ( $\text{Cl}_2$  or  $\text{HOCl}$ ) reacted with carbonaceous packing material in the adsorbent columns. Since chlorine has a very fast reaction rate in wastewater and all wastewater spike levels were below breakpoint concentration, there should have been no free chlorine available in spiked samples at the time of purging on to adsorbent columns. This was confirmed by completion of chlorine analysis on spiked wastewater samples after the 2 hour incubation period, as there was no chlorine residual observed in these samples after the incubation period.

**Table 5 Chloroform Concentrations in Chlorine-Spiked Wastewater and Distilled Water**

Spike Level (mg/L) of Chlorine	Volume of Sample Purged(mL)	Chloroform Concentration( $\mu\text{g/L}$ )
Municipal Wastewater		
2	10	15
5	10	32

10	10	46
50	10	133
100	5	320
Distilled Water		
5	10	10
10	10	10
50	10	86
Distilled Water with Sodium Sulfite		
5	10	Below Detection
50	10	Below Detection
5	10	Below Detection
50	10	Below Detection

### Examination of Carbotrap 300 Adsorbent Columns

The Carbotrap adsorbent columns were examined for reproducibility during preliminary experimentation. Six of the adsorbent columns were randomly selected from a group of 13 tubes and conditioned at 300°C for 2 hours to remove any residual compounds from previous analyses. An analysis blank was completed on each tube and no residual compounds were observed. Standard VOC mix 7/8 (500 ng) was then purged onto each tube individually, and tubes were then analyzed using thermal desorption (purge and trap) GC/MS analysis. Results are provided in Figure 11 and indicated less than a 5% variation in response between tubes 15, 13, 1 and 6 for all four trihalomethanes. Tube 4 showed a variation in response with respect to the previous four tubes for chloroform and increased the

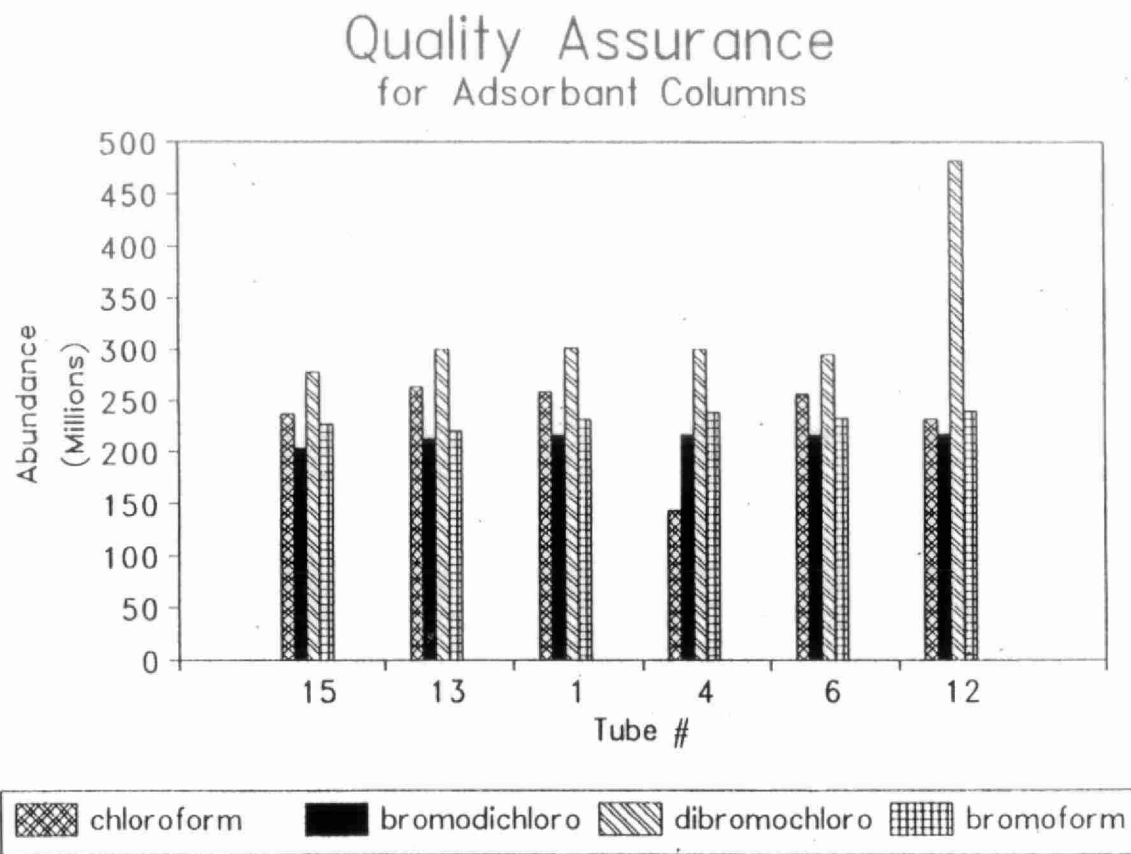
percent standard deviation for response to chloroform from 6% to 20%. Therefore tube 4 was not used for experimentation. Tube 12 showed relatively high response to dibromochloromethane and comparable responses, with respect to tubes 15, 13, 1 and 6, to the other three trihalomethanes. The response to dibromochloromethane from tube 12 increased the percent standard deviation in response from 3% to 23%. For this reason tube 12 was also not used for experimentation. Tubes 15, 13, 1 and 6 were therefore labelled and stored separately from the other columns so no cross contamination would occur from other experimentation in the laboratory.

During final experiments (experiments 10 to 17), the standard VOC mix 7/8 (500 ng) was injected onto two Tenax adsorbent columns to ensure consistency between the tubes. Less than 10% variation between the columns for all compounds occurred, and these two columns were used for final experimentation.

### **Methodology for the Purge and Trap Unit**

The method used for the purge and trap unit during preliminary experiments employed a three minute bake at the end of a desorb mode. To ensure that all compounds were removed from the adsorbent columns during the desorb mode a standard VOC mix 7/8 (500 ng) was purged onto an adsorbent column. This column was run on the purge and trap unit without the bake mode. This allowed for further analysis of the adsorbent column for residual compounds after the desorb mode. The adsorbent column was run again using the same desorb time

Figure 11      Quality Assurance (Adsorbent Columns)



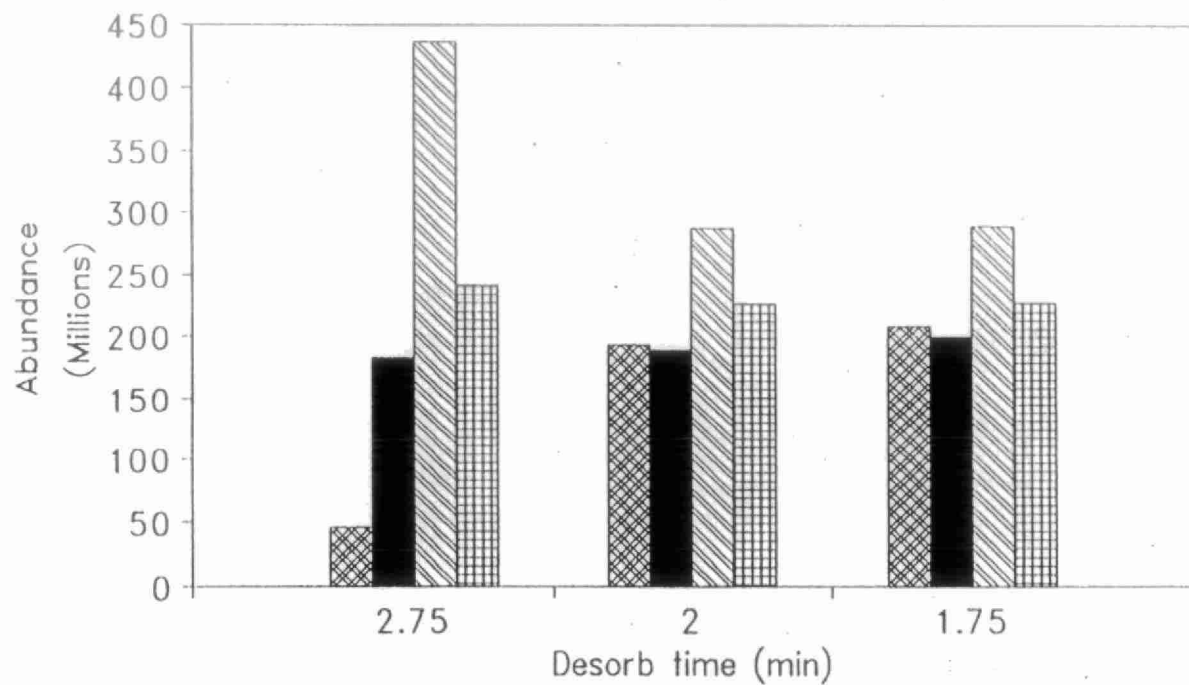


and temperature. No compounds were observed on the adsorbent column on the second run. It was therefore assumed that all compounds of interest were desorbed with the method described and no residue was left on the columns.

To optimize the methodology of the purge and trap unit, various desorb times were examined. Figure 12 shows how variations in the desorb time affected the mass spectrometer response to four trihalomethanes. A desorb time of 2.75 minutes maximized the response of dibromochloromethane. A desorb time of 2.0 minutes appeared to optimize the response of all four compounds of interest. A desorb time of 1.75 minutes also appeared to optimize the response of these compounds, but it was felt that this desorb time might be too short to ensure removal of all compounds from the adsorbent column. At a 2.75 minute desorb time, the peak shape of chloroform was much broader than at the shorter desorb time. This broadening of the peak caused the appearance of a lower response to chloroform as the software used with the GC/MS would recognise a broad peak as two separate compounds. During preliminary experiments, all four trihalomethanes were examined. Therefore, a desorb time of 2.0 minutes was used for all preliminary formation experiments.

For final experiments, the purge and trap unit was again optimized. It was observed that chloroform response was optimized using the Tenax adsorbent columns using a lower purge gas flow and a longer desorb time. Therefore, a desorb time of 2.75 minutes was used for final experiments.

## Quality Assurance Optimization of Purge and Trap



Chloroform Bromodichloro Dibromochloro Bromoform

Figure 12 Quality Assurance (Desorb Time for Columns)

#### 4.1 Background Levels of Chloroform in Guelph Wastewater

Physical and chemical characteristics of untreated wastewater used for each experiment are summarized in Table 6. Levels of chloroform observed in City of Guelph wastewater varied from below detection to 35  $\mu\text{g/L}$ . The level of chloroform in raw wastewater samples was determined during each sampling event by the method described in section 3.2. There appeared to be no relationship between wastewater characteristics and the level of chloroform observed in raw wastewater. Table 7 shows the R-squared values found from the linear regression analyses completed on the plots of chloroform in raw wastewater versus wastewater characteristics and formation factors.

**Table 6: Levels of Chloroform ( $\mu\text{g/L}$ ) in Raw Wastewater for Each Sampling Event (including wastewater characteristics)**

Event	Chloroform in Raw WW ( $\mu\text{g/L}$ )	$\text{NH}_3$ mg/L	TSS mg/L	VSS mg/L	pH
1	BD	31	216	NA	7.0
2	2	24	257	NA	7.1
3	2	24	298	NA	7.1
4	1	38	226	NA	7.5
5	7	24	383	NA	7.3
6	3	30	226	NA	NA
7	35	18	241	NA	8.2

8	14	35	206	148	8.4
9	BD	37	329	238	8.4
10	35	27	448	195	8.2
11	BD	29	268	224	8.2
12	BD	23	129	103	8.3
13	1	35	238	200	8.3
14	1	22	216	172	8.1
15	5	27	308	245	8.1
16	25	19	149	117	7.9
17	8	23	203	154	7.9
Average	8				

**Table 7: R-Squared Values for Plots of Chloroform in Raw Wastewater Samples versus Wastewater Characteristics and Formation Factors**

Plot Variables	R-Squared Value for Plot
Chloroform Concentration in Raw Wastewater versus Formation Factors	0.001
Chloroform Concentration in Raw Wastewater versus Ammonia Concentration	0.190
Chloroform Concentration in Raw Wastewater versus Total Suspended Solids Concentration	0.055
Chloroform Concentration in Raw Wastewater versus pH	0.075

## 4.2 Formation Factors

Chloroform formation factors (FF) for all preliminary and final experiments are listed in Table 8. Formation factors were calculated from a least-squares linear regression of the plot of chloroform concentration versus chlorine spike level. Formation plots are provided in Appendix F.

The chloroform concentration observed in unspiked wastewater samples was subtracted from the chloroform concentration observed in each spiked sample. This corrected for any error that would arise in the calculation due to pre-existing chloroform in the raw wastewater. This background correction was followed by completion of linear regression analyses on chloroform formed ( $\mu\text{g/L}$ ) versus concentration of chlorine spike ( $\text{mg/L}$ ), where the best-fit line was forced through zero. Thus, formation factors represent the slopes of the linear regression equations. Also shown in Table 8 are the  $R^2$  values associated with each regression analysis.

Formation factors ranged from 0.43 to 4.26  $\mu\text{g/mg}$ , with an arithmetic mean of 1.4  $\mu\text{g/mg}$ . The geometric mean was calculated to be 1.3  $\mu\text{g/mg}$ . The modal range was <0.8 to 1.0  $\mu\text{g/mg}$ . This implies that a higher frequency of formation factors had values lower than 1.4  $\mu\text{g/mg}$ , with larger formation factor values skewing the mean to a larger value. Figure 13 indicates the cumulative distribution plot for all of the formation factors observed. This plot indicates that 80% of the formation factors were in the range of 0.5  $\mu\text{g/mg}$  to 1.8  $\mu\text{g/mg}$ . The plot also indicates that the cumulative distribution is of a lognormal nature.

**Table 8: Sampling Event with Associated Formation Factors**

Sampling Event	Date	Formation Factor* (FF)	R Squared
1	Sept 16/91	+0.55	0.967
2	Sept 30/91	+0.85	0.859
3	Oct 1/91	+0.58	0.997
4	Oct 5/91	+0.55	0.998
5	Oct 7/91	+0.92	0.985
6	Oct 9/91	+0.93	0.980
7	Nov 1/91	+1.92	0.507
8	Nov 13/91	+1.52	0.960
9	Dec 8/91	+1.06	0.990
10	Dec 11/91	+0.77	0.822
11	Dec 15/91	+0.37	0.905
12	Jan 18/92	+4.33	0.997
13	Jan 22/92	+3.06	0.889
14	March 23/92	+1.66	0.958
15	March 26/92	+0.65	0.980
16	April 24/92	+3.14	0.973
17	April 26/92	+1.36	0.960
average		1.40	
standard deviation		1.02	

\*Formation Factor: in units of  $\mu\text{g}$  of chloroform formed/ mg chlorine spiked (as  $\text{Cl}_2$ ).

The 99% confidence interval about the formation factor sample mean is 0.62 to 2.1  $\mu\text{g}/\text{mg}$ . This range encompasses formation factors reported for several other studies involving untreated wastewater. From the studies completed on chloroform formation in raw wastewater, the following average formation factors were obtained:

This study	1.40 $\mu\text{g}/\text{mg}$
Chou (1990)	1.45 $\mu\text{g}/\text{mg}$
Cooper <i>et al.</i> (1977)	1.95 $\mu\text{g}/\text{mg}$
Dore <i>et al.</i> (1982)	1 $\mu\text{g}/\text{mg}$

These formation factors have an average of 1.43  $\mu\text{g}/\text{mg}$  with a sample standard deviation of 0.39  $\mu\text{g}/\text{mg}$ . Thus, these values are statistically equivalent within a 95 percent confidence interval. This implies that results obtained for chloroform formation factors using raw municipal wastewater were the same even though the studies were completed in different cities. Therefore the results of this study and the other three studies reported above may be reasonably used in other areas for chloroform formation estimations in raw wastewater.

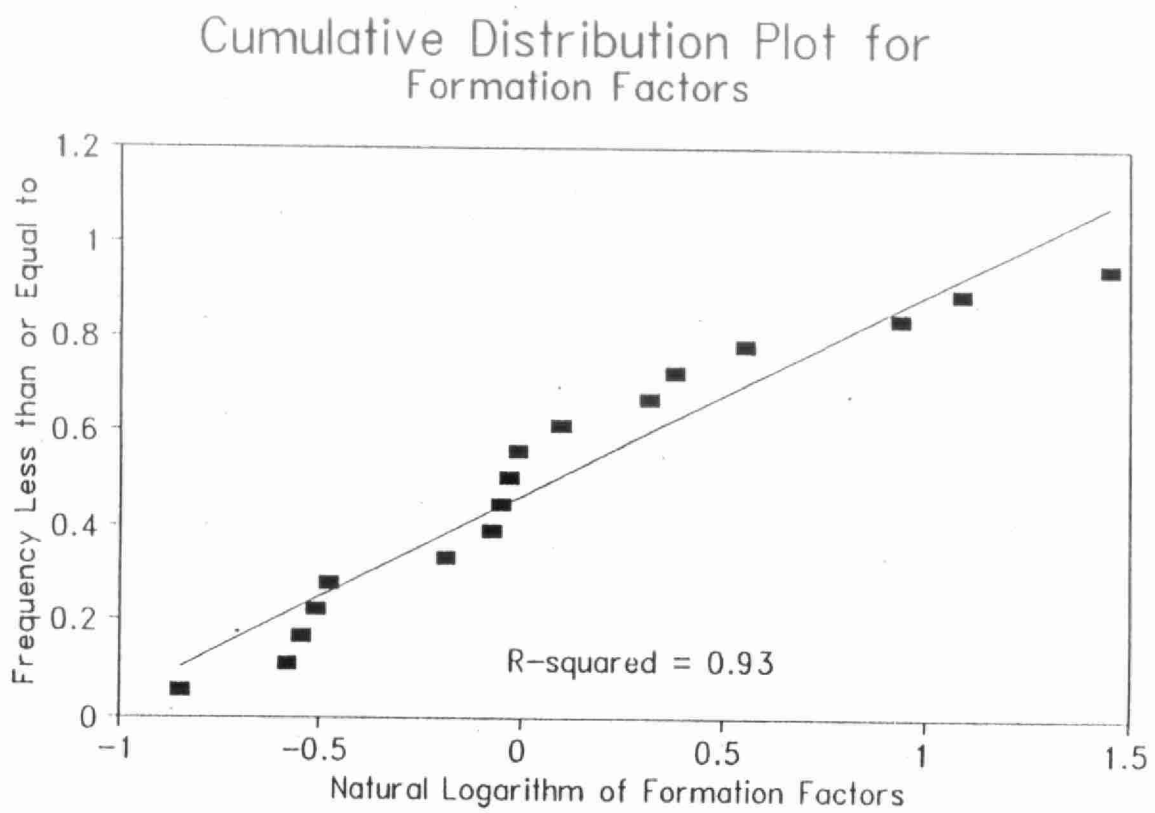


Figure 13 Cumulative Distribution Plot for Formation Factors



### 4.3 Effects of Wastewater Characteristic on Formation Factors

Figures 14 to 17 consist of plots of wastewater characteristics versus formation factor. Figure 14 provides a plot of formation factor versus total suspended solids concentration.

**Table 9: Sampling Event and Wastewater Characterization**

Event	FF	NH <sub>3</sub> mg/L	TSS mg/L	VSS mg/L	pH
1	0.55	31	216	* NA	7.0
2	0.85	24	257	NA	7.1
3	0.58	24	298	NA	7.1
4	0.55	38	226	NA	7.5
5	0.92	24	383	NA	7.3
6	0.93	30	226	NA	NA
7	1.92	18	241	NA	8.2
8	1.52	35	206	148	8.4
9	1.06	37	329	238	8.4
10	0.77	27	448	195	8.2
11	0.37	29	268	224	8.2
12	4.33	23	129	103	8.3
13	3.06	35	238	200	8.3
14	1.66	22	216	172	8.1
15	0.65	27	308	245	8.1
16	3.14	19	149	117	7.9
17	1.36	23	203	154	7.9
average	1.40	27	255	180	7.6
std deviation	1.02	6.1	80	49	0.5

\* NA = not analyzed

An R squared of 0.36 was observed from the linear regression of formation factor versus total suspended solids. An R squared of 0.51 was then obtained from the linear regression of formation factor versus the natural log of total suspended solids concentration. This suggests that there may be an inverse exponential relationship between formation factor and TSS. Further investigation would be necessary to verify this observation.

Again, an inverse trend was observed when VSS was plotted against the formation factor (Figure 15). An R squared of 0.63 was obtained from the linear regression of this plot. This was the best correlation obtained for any of the wastewater characteristics versus formation factor. However, this correlation is based on only 9 sets of data as volatile suspended solids was not measured during 8 of the experiments.

Formation factor versus pH is plotted in Figure 16. Kavanaugh *et al.* (1980) stated that the rate of formation increases with pH for reactions between chlorine and most precursors although some exceptions have been observed. However, it has also been observed that in wastewater reaction rates of chlorine with ammonia reach a maximum at pH 8.3 (Stenstrom *et al.*, 1987). Results of this study show that the highest formation factors do occur in the pH range of 8.3, although there did not appear to be a definite trend in formation factor above or below pH 8.3.

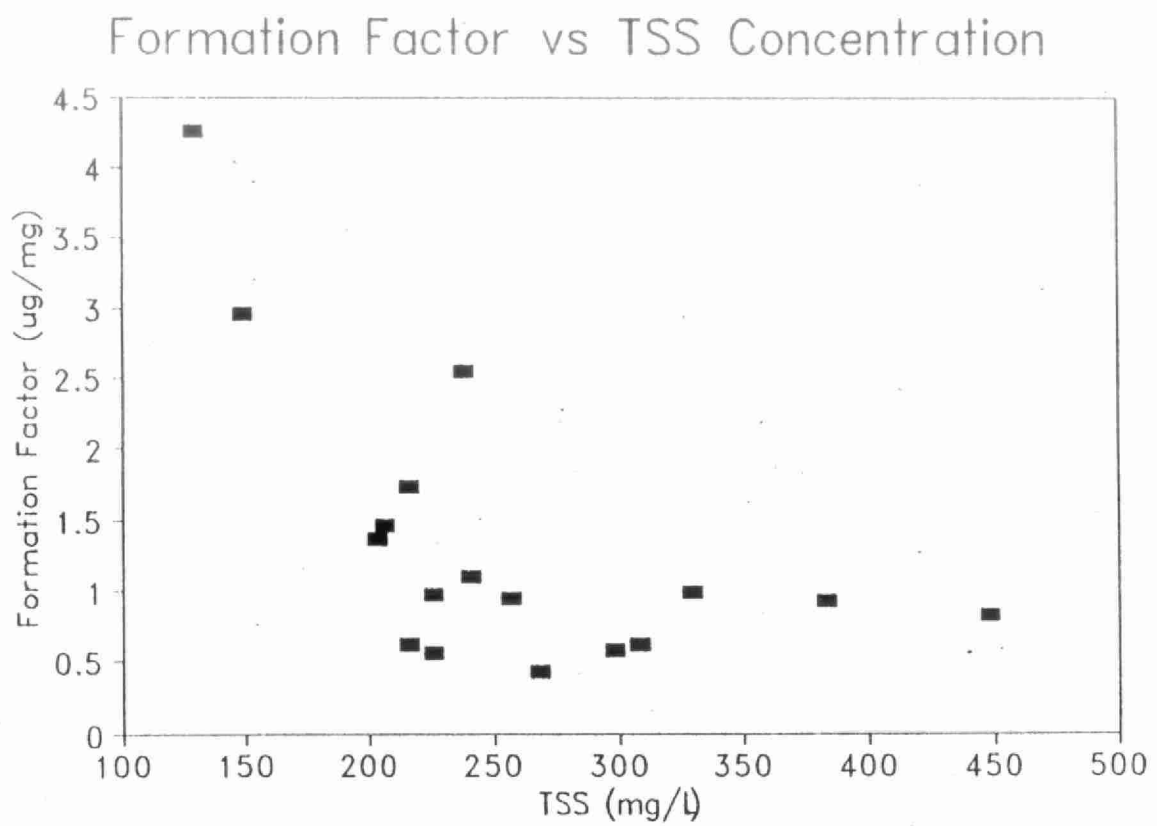
Chlorine reacts very rapidly with ammonia in wastewater thus reducing the

formation of chloroform. Figure 17 shows formation factor versus ammonia concentration in wastewater. The highest formation factors occurred at lower ammonia concentrations. This agrees with theory, i.e. chlorine reacts competitively with ammonia and organic precursors to form chloroform. However, there did not appear to be a definite trend in the formation factor with respect to ammonia concentration as the R squared value obtained from the linear regression of this plot was below 0.1. This could be explained by competing reactions, effects of pH and types of precursors present in the wastewater at any particular sampling event. Other reactions which occurred in the wastewater will mask the effects of ammonia on formation factors.

Linear regressions were also completed on a plot of formation factor versus the product of TSS and ammonia concentrations. This was done to eliminate the masking of any competing reactions between TSS and ammonia. An R squared value of 0.32 was obtained for this plot. This implies that there was little correlation between ammonia, TSS and formation factors obtained from this study.

Studies were completed to assess the relationship between pH and ammonia species on formation factors. Further studies were completed on the effects of pH and chlorine species on formation factors. No conclusive results were obtained from these studies.

Figure 14 Formation Factor versus Total Suspended Solids Concentration



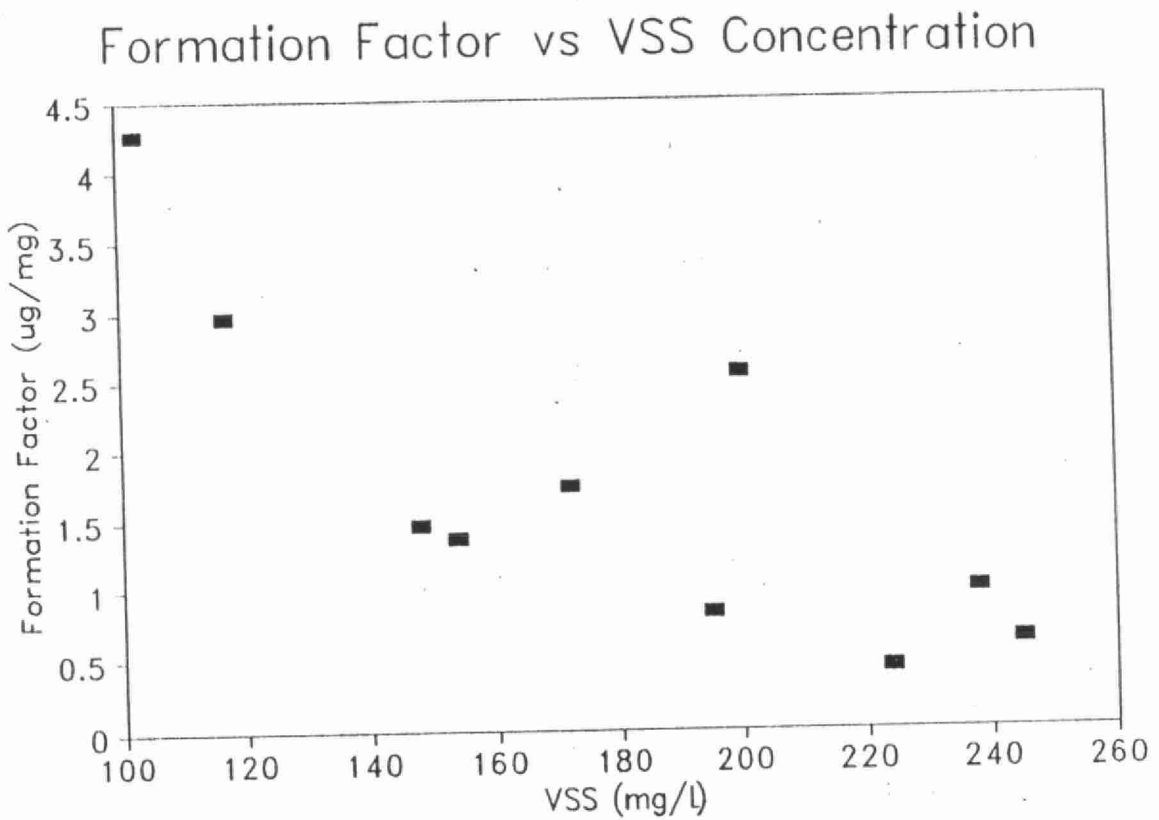
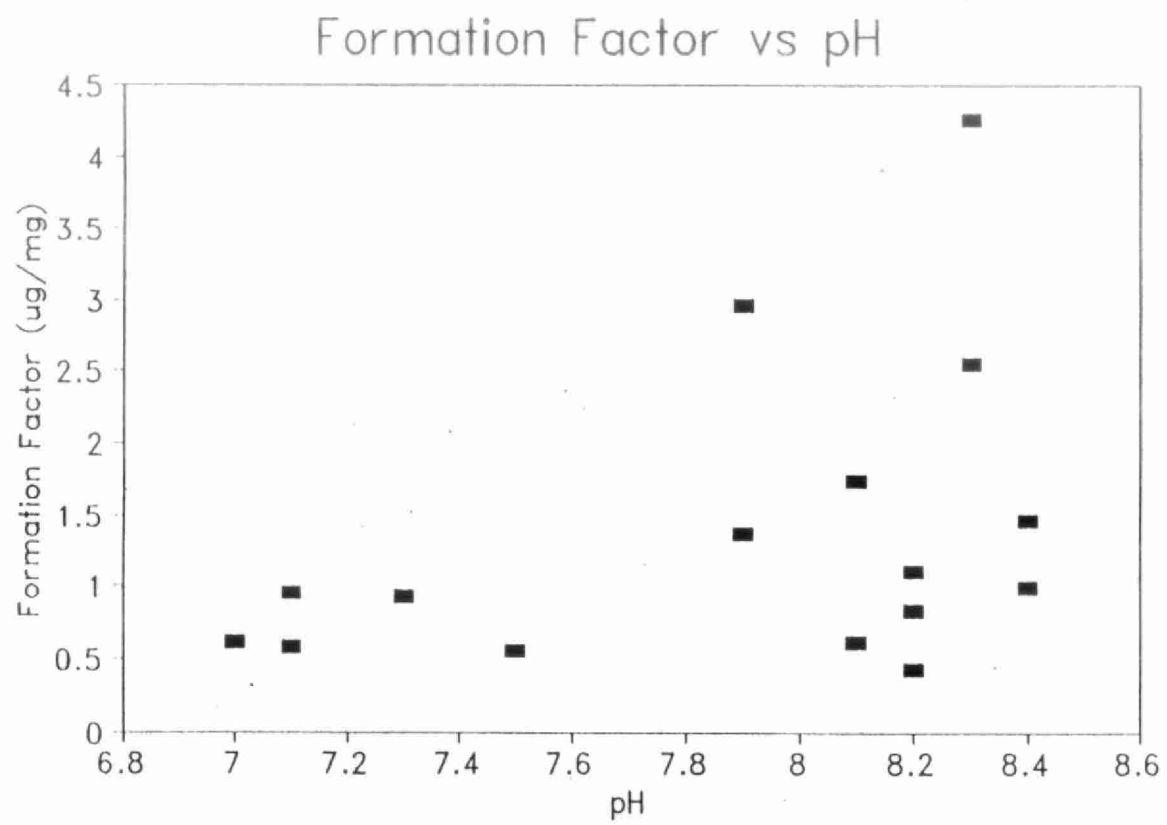


Figure 15 Formation Factor versus Volatile Suspended Solids Concentration

Figure 16 Formation Factor versus pH



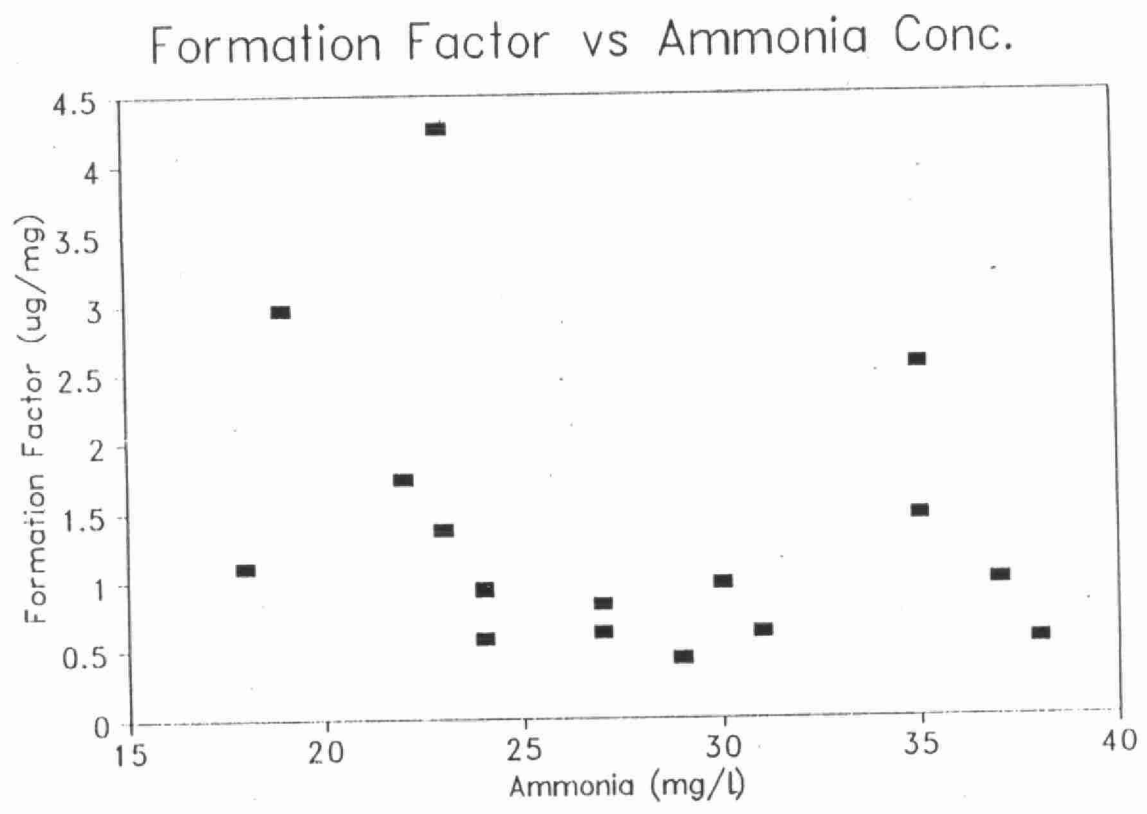


Figure 17 Formation Factor versus Ammonia Concentration

#### 4.4 Significance of Chloroform Formation Caused by Bleach Discharges

The average FF observed in this study ( $1.4 \mu\text{g}/\text{mg}$ ) was coupled with the chlorine use estimates for the City of Guelph (1 to  $1.5 \text{ mg}/\text{L}$ ) to obtain approximate chloroform yields. Based on this exercise, it is predicted that the use of chlorinated laundry detergents contributes approximately  $1 \mu\text{g}/\text{L}$  of chloroform to Guelph wastewater. The concentration of chloroform in raw wastewater at the headworks of the Guelph WWTF ranged from below detection to  $35 \mu\text{g}/\text{L}$  with an average of  $8.1 \mu\text{g}/\text{L}$ . On average the concentration of chloroform in Guelph drinking water is  $10 \mu\text{g}/\text{L}$  (Corsi *et al.*, 1992). This implies that the amount of chloroform formed in municipal wastewater from chlorine discharge in Guelph is low relative to that coming from potable water. However, the chloroform in Guelph potable water does not explain the levels of chloroform in raw municipal wastewater greater than  $10 \mu\text{g}/\text{L}$ . Large discharges of chlorine to the Guelph sewer system could account for the relatively high levels of chloroform observed in raw wastewater.

It is estimated from the aforementioned calculations that on a yearly basis 16 kg of chloroform would be formed in the Guelph sewer system. This compares with values calculated for the Toronto area of 560 kg, 1700 kg for Ontario and 5000 kg for all of Canada (Bridgman, 1992).

Assuming that this is an approximate yield for most residential/commercial wastewaters with characteristics similar to Guelph wastewater (see Tables 7 and 8), it is reasonable to conclude that in-sewer formation of chloroform is generally



small relative to levels of chloroform discharged to sewers in the form of chlorinated/potable drinking water (often in excess of 20–50  $\mu\text{g/L}$ ).

However, there will be immediate levels of chlorine entering sewer systems which exceed the estimated 1.0 to 1.5 mg/L of chlorine. Mop and pail solutions call for levels of chlorine to be at 300 mg/L for proper cleansing. When these solutions are discharged to a sewer system there can be levels at the point of entry that are much greater than 1.0 mg/L of chlorine. These will cause formation of chloroform in that area to be significantly higher than that which would have been estimated by use of the values calculated for chlorine in the wastewater at any given time. The mop and pail solutions or solutions used in other household cleaning and low energy dishwashers will react initially in use. In other words, if the recommended dosage of chlorine is 200 mg/L in a dishwasher, a portion of this chlorine will react in the dishwasher before it is discharged to the sewer system. Quantification of pre-discharge chlorine consumption was beyond the scope of this study.

## 5.0 SUMMARY AND CONCLUSIONS

Large quantities of domestic bleach containing sodium hypochlorite are sold in North America. A series of laboratory experiments was completed to determine chloroform formation factors following chlorinated bleach spiking of raw wastewater. Untreated municipal wastewater was chlorinated with concentrations ranging from 0 to 100 mg/L  $\text{Cl}_2$ , values which could be reached in sewers serving commercial bleach users.

The formation of chloroform was observed to be directly proportional to chlorine dose. Formation factors were calculated from the linear regression of this relationship and were observed to range from 0.4 to 4.3  $\mu\text{g}/\text{mg}$  with an average of 1.4  $\mu\text{g}$  chloroform per mg chlorine spike. Values of R-squared ranged from 0.786 to 0.999 reflecting a strong correlation between chlorine dose and chloroform formation.

Chloroform formation factors calculated in this study strongly agreed with those found in the literature. Formation factor values of 1.35  $\mu\text{g}/\text{mg}$  (this study), 1.45  $\mu\text{g}/\text{mg}$  (Chou, 1990), 1.95  $\mu\text{g}/\text{mg}$  (Cooper *et al.*, 1977), and 1  $\mu\text{g}/\text{mg}$  (Dore *et al.*, 1982) were observed in studies completed in different cities. These values are statistically the same within a 95 percent confidence interval.

Calculations were completed to assess the relevance of chloroform formed due to chlorine discharge relative to that discharged from potable drinking water. Chloroform formation in sewers is generally small relative to chloroform levels in

potable drinking water. It was found that the chloroform formed in sewers due to chlorine discharge was approximately 10 percent of that discharged from potable drinking water. It was also found that the chloroform formed in sewers was, on average, only about 13 percent of the chloroform observed in raw wastewater in Guelph.

Chloroform formation is influenced by wastewater characteristics. Wastewater characteristics were compared to chloroform formation due to chlorine discharge. It was found that the formation factors ( $\mu\text{g}$  chloroform formed/mg chlorine spike) varied inversely as the concentration of total and volatile suspended solids in the wastewater. It was also observed that formation factors reached a maximum at pH 8.3 which agreed with findings in the literature. There was a very poor correlation found between formation factors and ammonia concentrations in wastewater. This was possibly due to masking of the effects of ammonia concentration by competing reactions of chlorine.

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## 6.0 RECOMMENDATIONS

As stated in Section 5.0, the chloroform formed by chlorine bleach discharge to the sewer system is small compared to that discharged from potable water sources. Therefore, there is no immediate need for further research with regards to chloroform formation in municipal sewer systems.

It is recommended that field studies be completed. These studies should include monitoring of chloroform concentrations in wastewater upstream and downstream of known high chlorine discharge points in one or more sewer systems. Field studies will aid in determining how chlorine entering a sewer system actually affects the concentration of chloroform in the ambient atmosphere. This would be completed by recording chloroform concentrations in a sewer system before and after a high chlorine discharge point and in return any increase in ambient chloroform concentrations at or downstream from the discharge point.

Initial studies should include analyses of discharges from low energy dishwashers and washing machines to estimate actual quantities of chlorine entering a sewer system from such sources. By quantifying chlorine levels in the discharge from these sources an improved estimate of chloroform formation in municipal sewer systems may be obtained.

Field studies should be completed to assess chloroform concentrations in the sewers and the ambient atmosphere directly downstream of restaurants using low energy dishwashers, commercial laundries, private homes and industrial or

institutional discharges that utilize chlorine for bleaching or sterilizing.

Further studies should also be completed to assess the effects of ammonia, pH and total organic carbon levels on chloroform formation factors. These relationships would aid in determining how and when chloroform formation would be the greatest and how the levels of formation could be estimated and/or controlled. Such experiments were beyond the scope of this study.

Finally, it is recommended that further studies be completed on the formation of chloroform prior to bleach discharge to sewer systems (i.e. formation of chloroform in dishwashers and washing machines). Formation of chloroform prior to discharge to the sewer system may be higher than in wastewater because of the relative concentrations of ammonia and inorganic compounds. Formation of chloroform before discharge may account for the high levels of chloroform observed in raw municipal wastewater that could not be accounted for by potable drinking water.

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## Appendix A:

### METHODOLOGY FOR GAS CHROMATOGRAPHIC ANALYSIS WITH MASS SELECTIVE DETECTION

#### PRELIMINARY STUDIES (SCAN METHOD)

1) Chloroform: retention time = 4.38 min  
extract and integrate from 3.50 to 5.00 min

target ion 83  
qualifier ion 85 rel resp. = 132.10 pct. unc. (rel) = 60

linear curve fit

2) Bromodichloromethane: retention time = 6.63 min  
extract and integrate from 5.61 to 7.6 min

target ion 129  
qualifier ion 83 rel resp. = 492.2 pct. unc. (rel) = 20

linear curve fit

3) Dibromochloromethane: retention time = 9.14 min  
extract and integrate from 8.1 to 10.1 min

target ion 129  
qualifier ion 127 rel resp. = 74.2 pct. unc. (rel) = 20

linear curve fit

4) Bromoform: retention time = 11.54 min  
extract and integrate from 10.54 to 12.54 min

target ion 173  
qualifier ion 175 rel resp. = 48.2 pct. unc. (rel) = 20

linear curve fit

#### ACQUISITION PARAMETERS

Inlet: GC  
Tune file: MIDMASS.U

Acquisition mode: Scan

Temperature Information

Detector 280 C

Injector 250 C

Oven equilibrium time: 0.00 min

Oven maximum : 275 C

Initial temperature : 24 C

Initial time : 0.00 min

Level	Rate (C/min)	Final temp. (C)	Final time (C)	(min)
1	40.00		42	2.20
2	9.00	200		3.00
3	0.00			

Next run time : 23.21 min

MS Information:

Solvent delay : 2.20 min

EM absolute : False

EMV offset : 0.0

Resulting voltage : 1352.9

[Scan parameters]

Low mass : 25

High mass : 275

Sampling # : 2 A/D Samples 4

Threshold : 300

[Real Time Plot Parameters]

Plotting active : False

Time window : 10 min

Total ion max : 1000000

Data Analysis Parameters:

Percent Report Settings:

Sort by : Signal

Output Destination

Screen : No

Printer : Yes

File : No

Integration Events: AutoIntegrate

Generate Report During Run Method : No

Signal Correlation Window : 0.020

Qualitative Report Settings:

Peak Location of Unknown: Apex

Library to Search	Minimum Quality
DATABASE\NBS49K.L	0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination

Screen : No

Printer : Yes

File : No

Generate Report During Run Method: No

FINAL STUDIES (SIM METHOD)

Acquisition Parameters:

General Information:

Inlet : GC

Tune File : MID2.U

Acquisition Mode : Sim

Injector Information:

Injection Source : Manual

Temperature Information:

Detector : 280 C

Injector : 250 C

[Oven Parameters]

Oven equilibrium Time : 0.00 min

Oven maximum : 275 C

Cryo : Off

Oven : On

[Oven Program]

Initial Temperature : 24 C

Initial Time : 0.00 min

Level	Rate (C/min)	Final Temp. (C)	Final Time (min)
1	40.00	42	2.20
2	9.00	130	0.00
3	40.00	200	3.00

Next Run Time : 17.18 min

MS Information

Solvent Delay : 2.33 min

EM Absolute : False

EMV Offset : 0.0

Resulting Voltage : 1352.9

[Sim Parameters]

Group 1

Group ID : Group 1

Dwell Per Ion : 50 msec.

Low Resolution : Yes

Group Start Time : 2.33

Ion Plotted : 83.00  
Ions In Group : 83.00 85.00 127.00 129.00 171.00  
173.00 175.00 252.00 257.00

[Real Time Plot Parameters]

Plotting Active : True  
Time Window : 13 min  
Total Ion Max : 10000000  
Ion Max : 50000000

Run Table Entries

State (MS on/off)	Time (min)
Off	13.00

Data Analysis Parameters

Percent Report Settings

Sort by : Signal

Output Destination

Screen: No  
Printer: Yes  
File: abundanc

Integration Events : AutoIntegrate

Generate Report During Run Method: Yes  
Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search Minimum Quality  
C:\DATABASE\NBS49K.L 0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination

Screen: No  
Printer: Yes  
File: No

Generate Report During Run Method: No

Quantitative Report Settings

Report Type: Summary

Output Destination  
Screen: No  
Printer: Yes  
File: quant.xls

Generate Report During Run Method: Yes

Compound Information:

1) Chloroform: retention time = 4.20 min  
extract and integrate from 3.50 to 5.00 min

target ion: 83.00  
qualifier ion: 85.00 rel resp. 70 pct. unc. (rel) 20.0  
lowboil.e

Linear curve fit

2) Bromodichloromethane: retention time = 6.63 min  
extract and integrate from 5.61 to 7.61 min

target ion: 129.00  
qualifier ion: 83.00 rel resp. 561.90 pct. unc. (rel) 20.0  
lowboil.e

Linear curve fit

3) Dibromochloromethane: retention time = 9.15 min  
extract and integrate from 8.00 to 10.00 min

target ion: 129.00  
qualifier ion: 127.00 rel resp. 0.00 pct. unc. (rel) 20.0  
lowboil.e

Linear curve fit

4) Bromoform: retention time = 11.53 min  
extract and integrate from 10.50 to 12.50 min

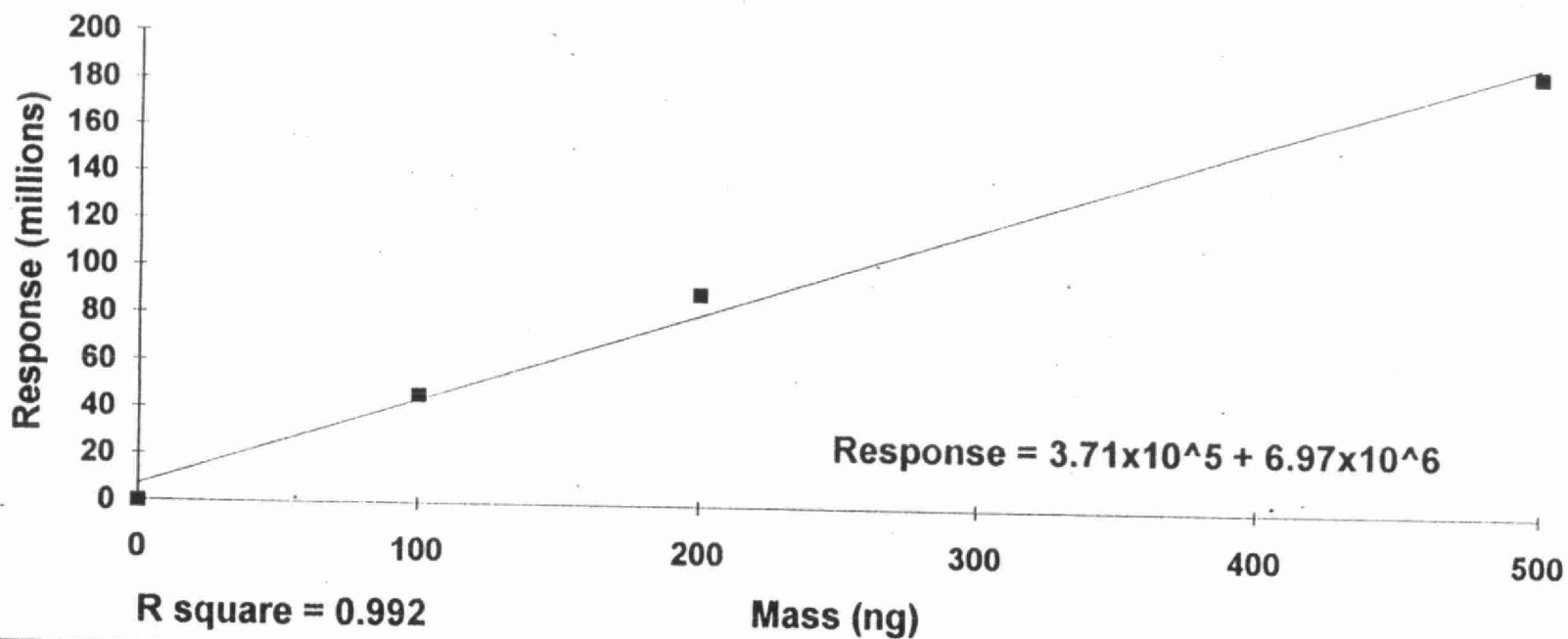
target ion: 173.00

qualifier ion: 175.00 rel resp. 47.90 pct. unc. (rel) 20.0  
lowboil.e

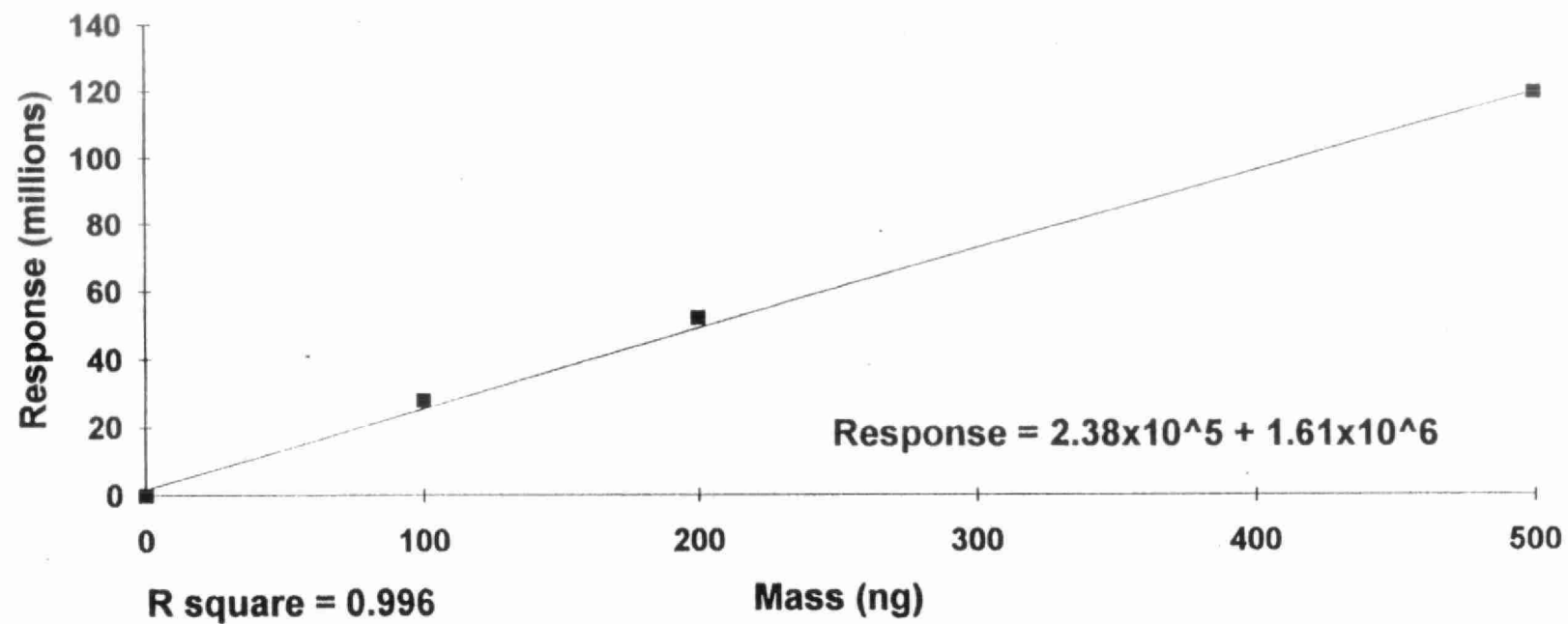
Linear curve fit



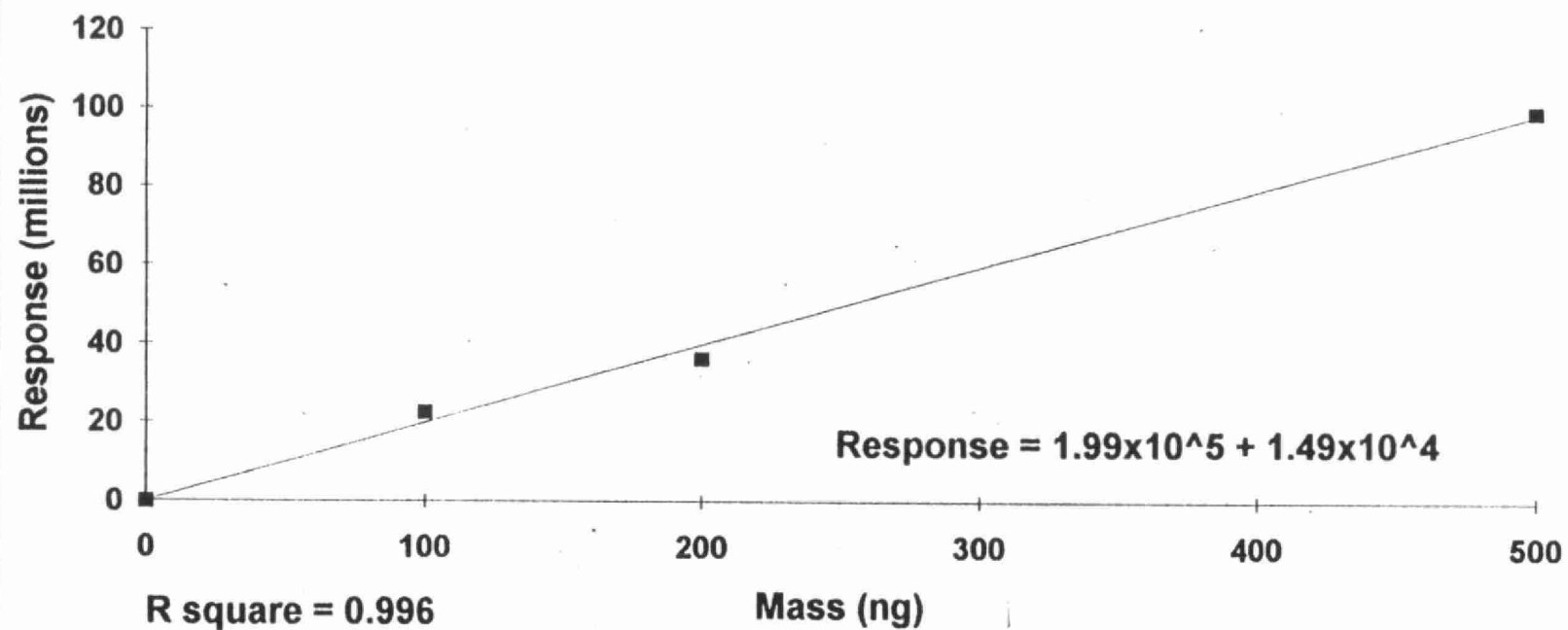
Calibration for Chloroform  
September 16, 1991



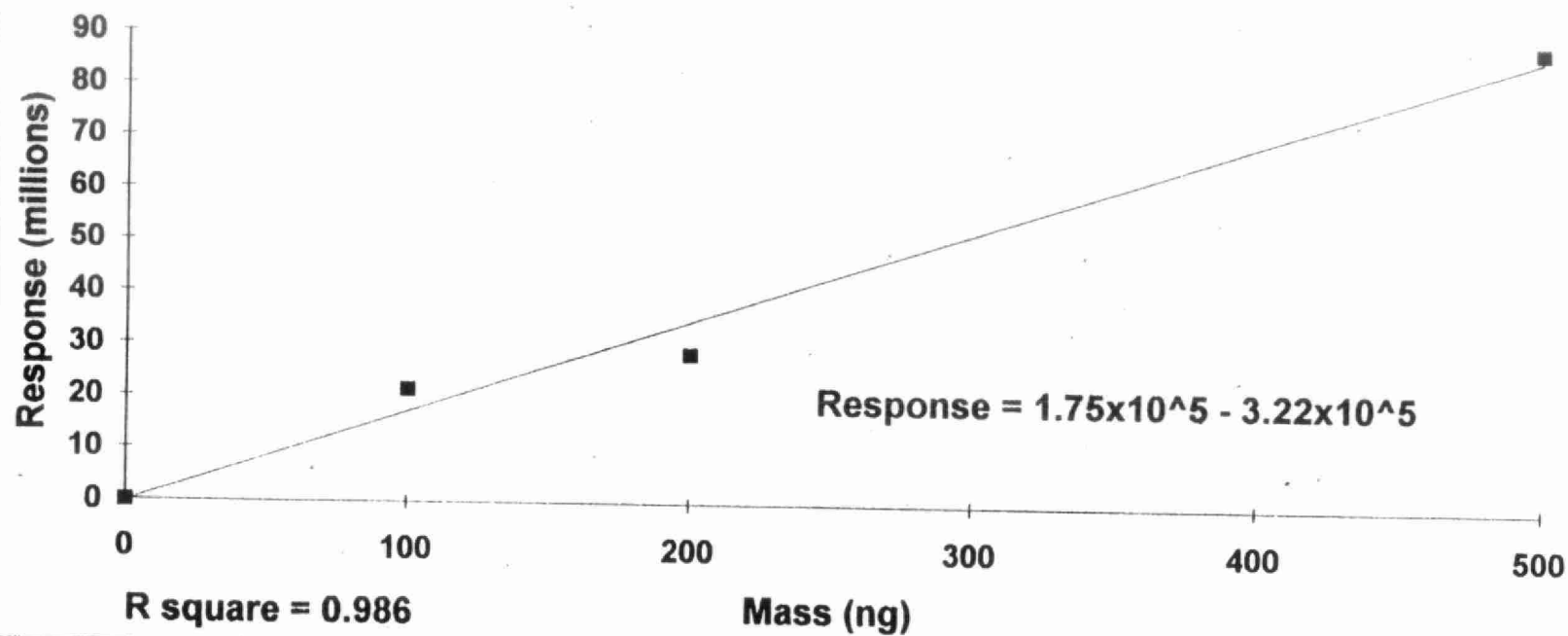
**Calibration for Chloroform**  
**September 30, 1991**



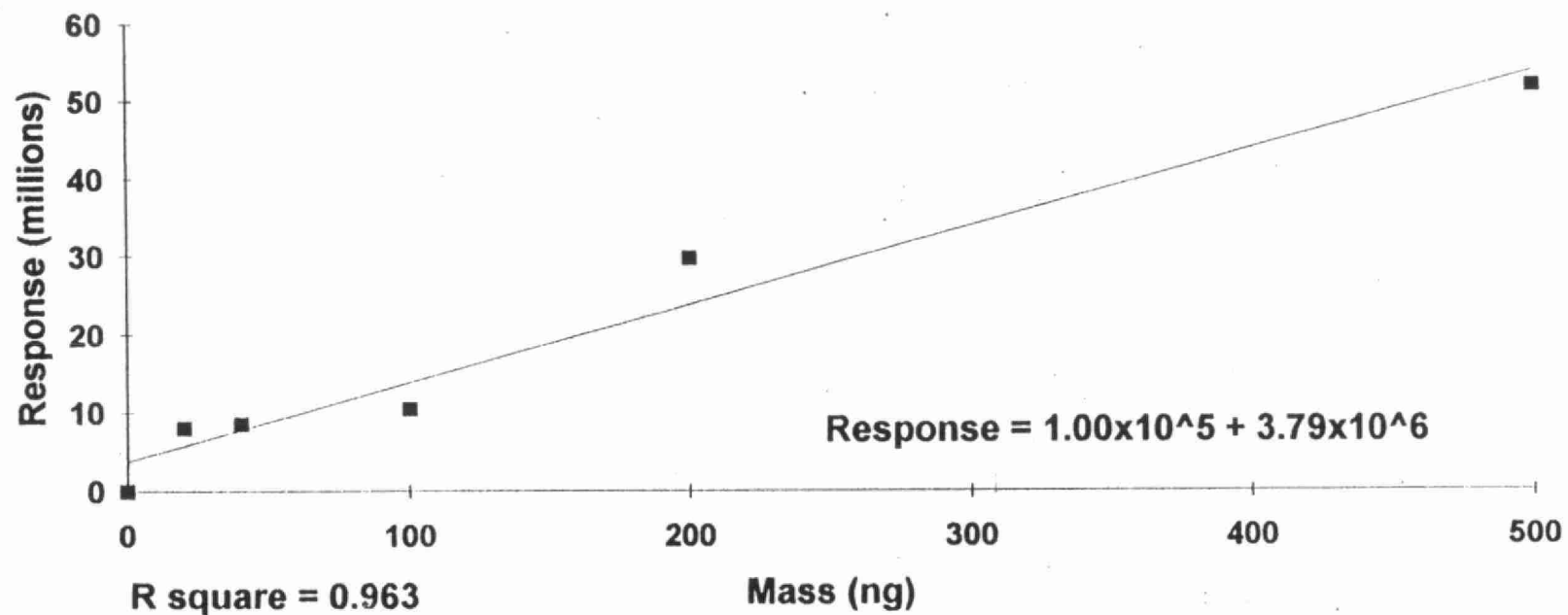
**Calibration for Chloroform  
October 1, 1991**



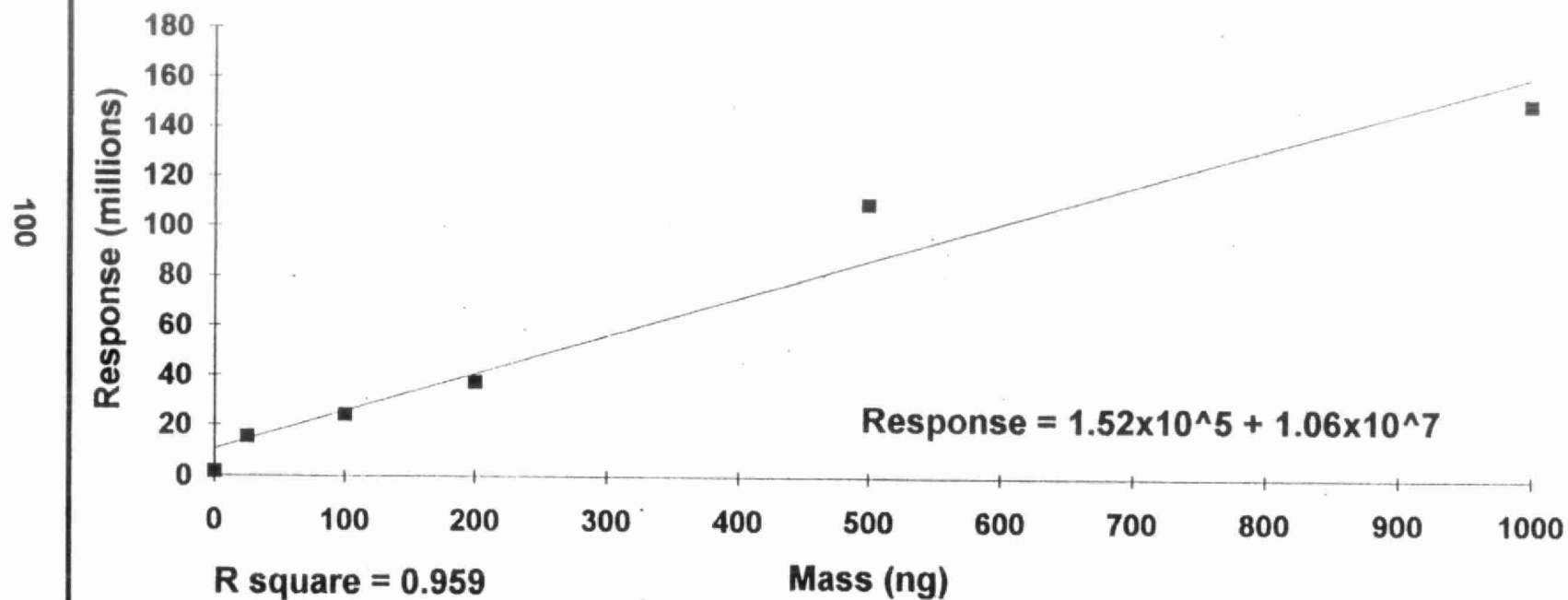
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**October 9, 1991**



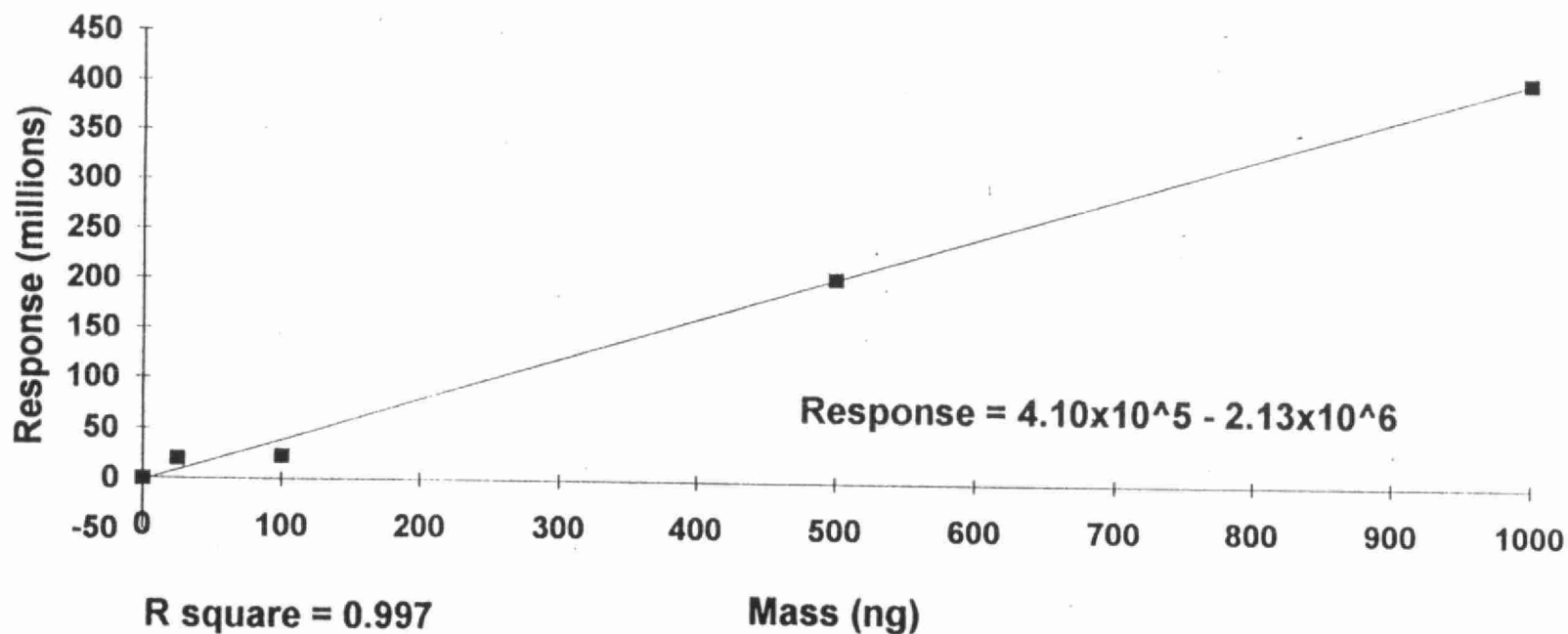
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November 13, 1991**



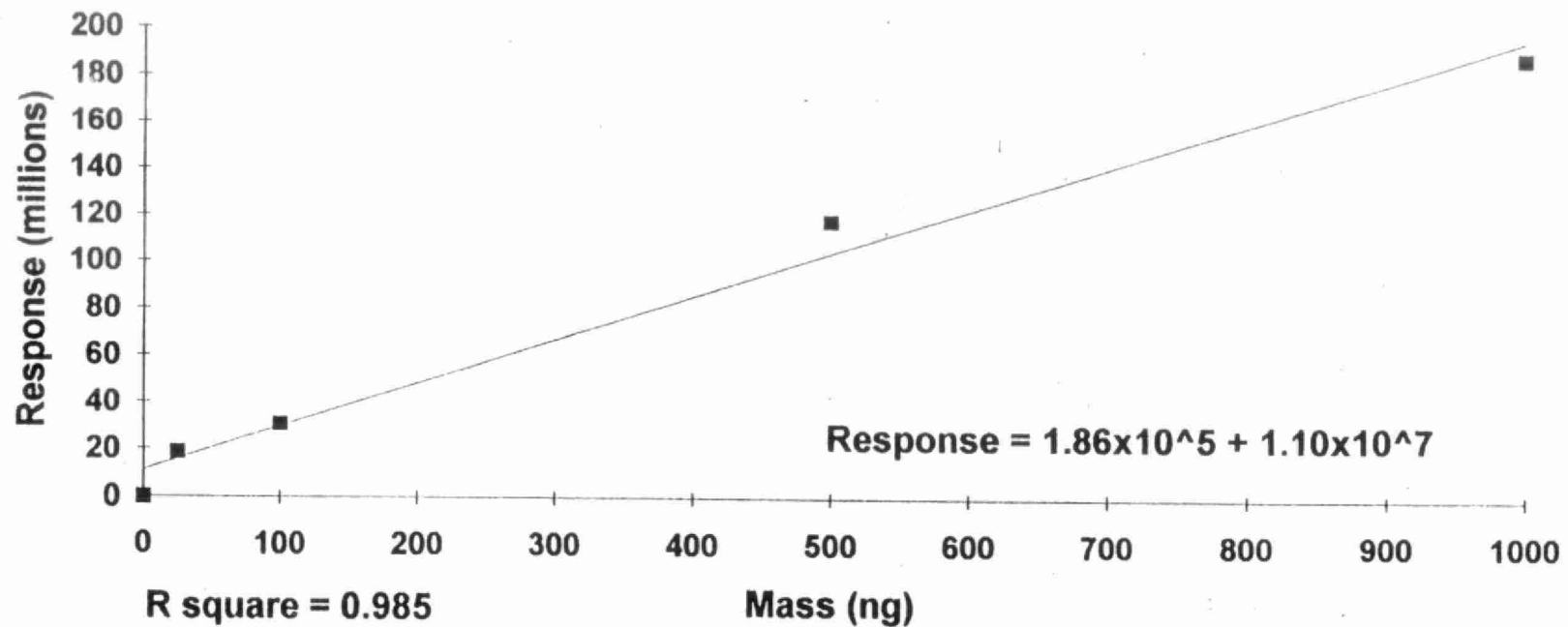
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**December 8, 1991**



**Calibration for Chloroform  
December 11, 1991**

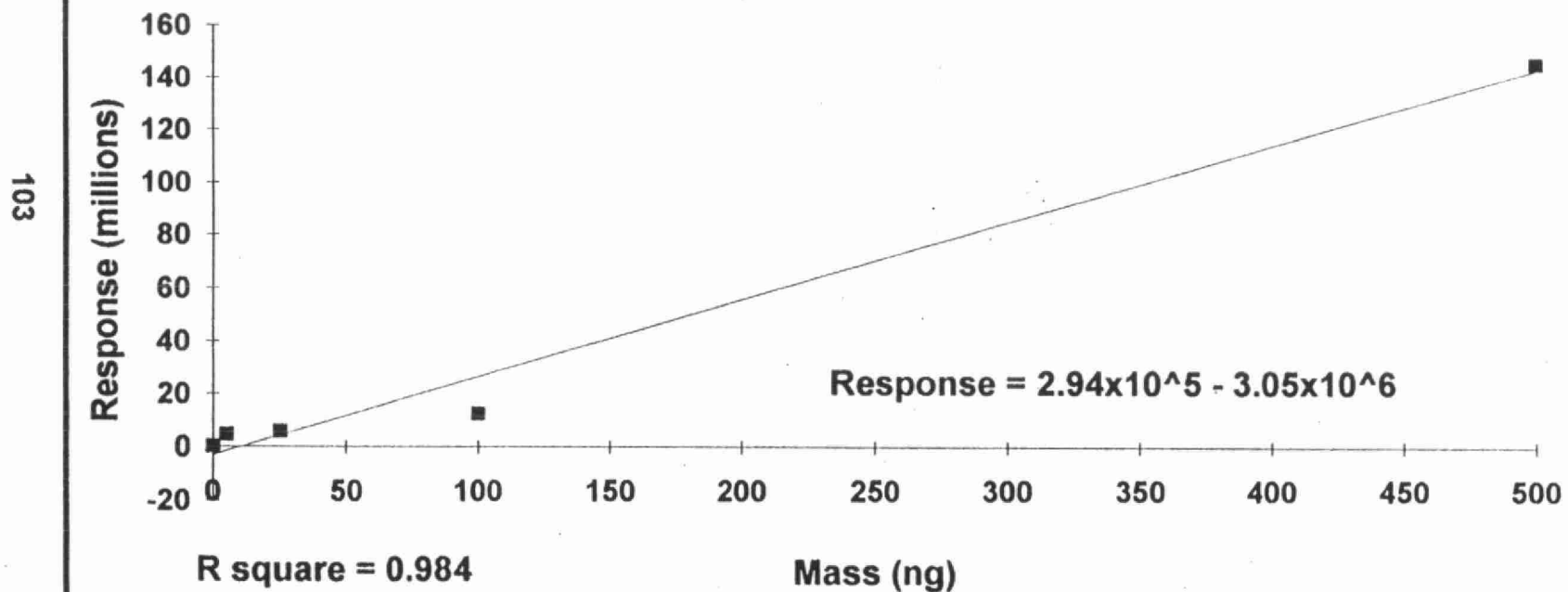


**Calibration for Chloroform**  
**December 15, 1991**

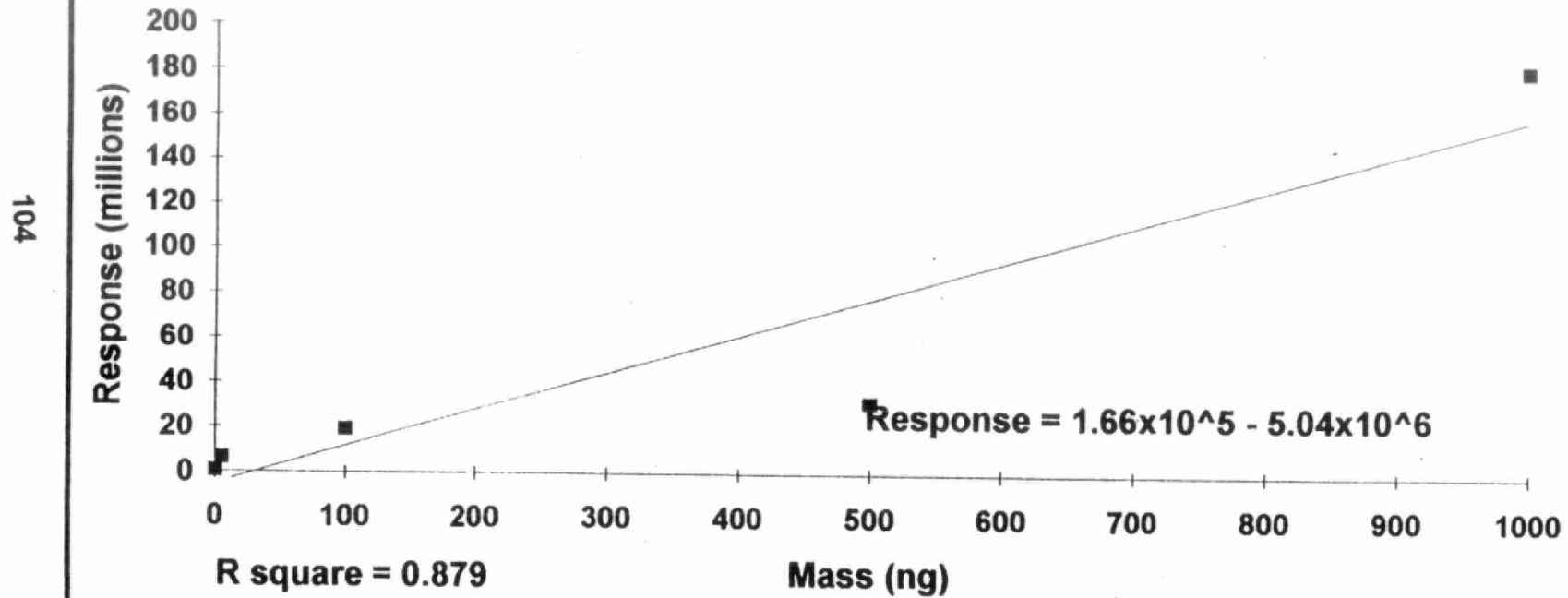




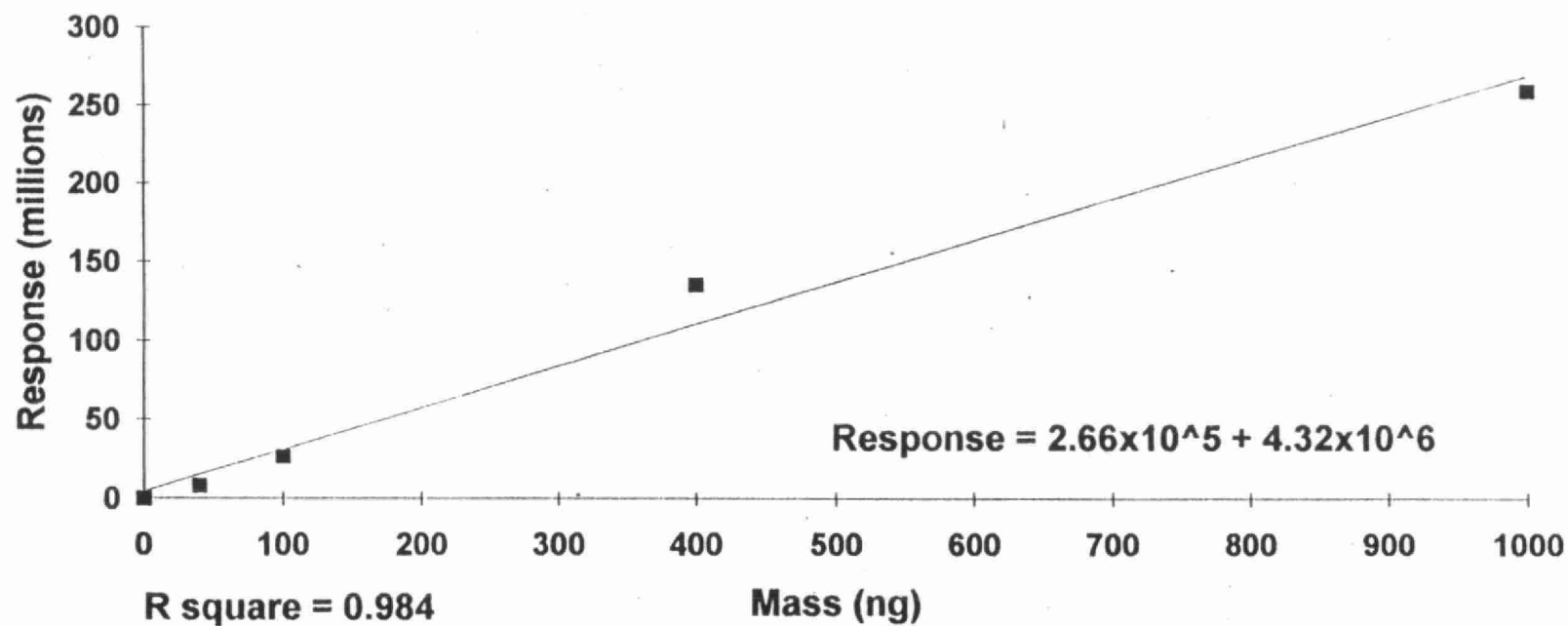
**Calibration for Chloroform**  
**January 18, 1992**



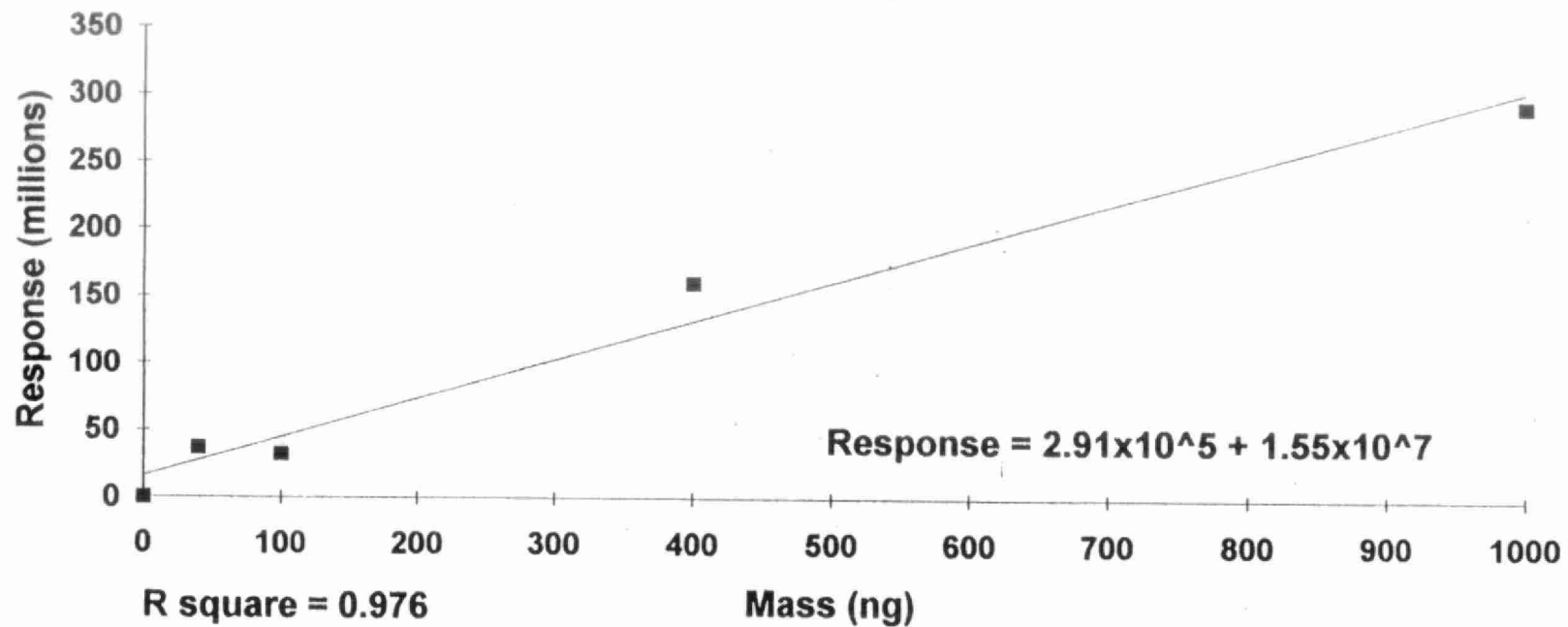
**Calibration for Chloroform**  
**January 22, 1992**



**Calibration for Chloroform**  
**March 23, 1992**



**Calibration for Chloroform**  
**April 24, 1991**



**APPENDIX C:     CHLORINE CONSUMPTION IN GUELPH BASED ON**  
**VALUES OBTAINED FROM BRIDGMAN (1992).**

1.     Total low temperature dishwashers presently in Guelph  
      20 (est.) with tabling, 1.7 gallons/cycle at 100 ppm.  
      50 (est.) under counter, 1.7 gallons/cycle at 100 ppm.
- 1a.    Total glasswashers using 1.5 gallons/cycle at 100 ppm.  
      30 (est.). Average run time of rinse, 60 minutes/day.
2.     Manual warewashing 10 gallons/sink at 100 ppm. 50 (est.)
3.     Mop pail solutions 300/day (est.) 4 gallons/pail at 300 ppm.
4.     Sanitizing solution 500/day (est.) 1 gallon/pail at 200 ppm.
5.     Chlorinated detergent used in high temperature dishwashers, 0.5  
      gallons/rack at 50 ppm. (each rack will accommodate 3.5 meals, or  
      customers).
6.     Commercial/Institutional use 15 gallons at 70 ppm/45 pounds of wash linen  
      (dry weight).  
  
      Residential uses 10 gallons at 200 ppm/load.

#### APPENDIX D: PROCEDURE FOR AMMONIA ANALYSIS

Distillation:

a) Borate buffer solution:

88 ml of 0.1 N NaOH solution was transferred to 500 ml of 0.025N  $\text{Na}_2\text{B}_4\text{O}_7$  solution (9.5g of sodium borate  $\cdot 10\text{H}_2\text{O}$ /L) in a 1.0 L volumetric flask and diluted to 1.0 L with distilled water.

b) Sodium hydroxide (6 N):

240 g of NaOH pellets were dissolved in 1.0 L of distilled water in a 1.0 L volumetric flask.

c) Dechlorination agent:

0.9 g of sodium sulfite was dissolved in distilled water to 1.0 L in a 1.0 L volumetric flask and prepared fresh daily.

d) Indicating boric acid receiving solution:

1) Mixed indicator solution: 200 mg of methyl red indicator was dissolved in 100 ml of 95% isopropyl alcohol in a 100 ml volumetric flask, 100 mg of methylene blue was dissolved in 50 ml of 95% isopropyl alcohol in a 50 ml volumetric flask, the solutions were combined and prepared fresh monthly.

2) Boric acid solution: 20 g of  $\text{H}_3\text{BO}_3$  was dissolved in 800 ml of distilled water and 10 ml of mixed indicator solution was added. The solution was diluted to 1.0 L with distilled water in a 1.0 L volumetric flask. This solution was prepared monthly.

Solutions were stored in 1.0 L tinted glass reagent bottles.

## PROCEDURE

In a 1.0 L round bottom flask, 500 ml of dechlorinated sample (wastewater samples were assumed to be dechlorinated as no free chlorine was present in the samples) was neutralized to pH 7.0 with either 1.0 N NaOH or 0.4 N H<sub>2</sub>SO<sub>4</sub> determined using a pH meter. If ammonia concentrations were expected to be less than 100 mg/l, 1000 ml samples were used. To the sample, 25 ml of borate buffer was added using a 50 ml graduated cylinder and the pH was adjusted to 9.5 with 6 N NaOH again using a pH meter. Using phenolphthaleine as an indicator, NaOH was added to the sample drop by drop until the colour of the solution became bright pink. When the colour changed, it was assumed that the pH of the solution was over 9.5. Using phenolphthaleine allowed visual confirmation that the wastewater sample remained over pH 9.5 throughout the distillation stage without the use of a pH meter.

Samples were transferred to the distillation apparatus illustrated in Figure 4 and distilled at a rate of 6–10 ml/min ensuring the tip of delivery tube was below the surface of the acid receiving solution. At least 200 ml of distillate was collected in a 500 ml erlenmyer flask which contained 50 ml of indicating boric acid receiving solution.

The distillate was neutralized with 1 N NaOH and titrated with standard 0.02 N H<sub>2</sub>SO<sub>4</sub> titrant until the indicator turned a pale lavender. A blank was carried through all steps of the procedure and the necessary correction was applied to the results.

The concentration of ammonia was calculated as follows:

$$\text{mg ammonia/ L} = (A-B) \times 280/\text{ml of sample}$$

A = volume of H<sub>2</sub>SO<sub>4</sub> titrated for sample

B = volume of H<sub>2</sub>SO<sub>4</sub> titrated for blank

## **APPENDIX E: GAS CHROMATOGRAPHY WITH MASS SELECTIVE**

### **DETECTION**

Chromatographic techniques make use of a stationary phase and a mobile phase where components of a mixture are carried through the stationary phase by the flow of the mobile one. Separations are based on differences in migration rates among the sample components. In gas chromatography the mobile phase is a gas (Skoog (1985)).

Compounds that have different solubilities in the liquid (stationary) phase of the gas chromatographic (GC) column will take different times to traverse the length of the column in the mobile phase. For a specific set of experimental conditions, the time it takes a compound to travel through a GC column is a physical property of that substance – called its retention time. Generally, less volatile compounds will have a greater retention time than more volatile compounds. Chloroform will have a relatively low retention time compared to other trihalomethanes. Because chloroform is more volatile than bromodichloromethane, dibromochloromethane and bromoform it will elute (i.e. pass through the column) before these compounds.

Substances that have a similar polarity to that of the liquid phase will be more soluble in the phase and will have a greater retention time than substances less soluble in the liquid phase. Therefore, organic compounds in a mixture can be separated from each other by using gas chromatography, and the retention times of these compounds can be used to assist in their identification (Clement, 1989).



As compounds are separated they can be detected using a mass selective detector. Molecules enter the source chamber of the mass selective detector which is maintained under high vacuum and are then bombarded by a high energy beam of electrons. The energy transferred causes the molecules to fragment and to ionize into positive ions by removal of an electron. These ions may be singly or multiply-charged. The positive ions formed are detected by a device which is able to count the number of ions which strike it. By plotting the abundance of ions detected versus their mass-to-charge ratio, a mass spectrum is obtained (Pavia *et al.*, 1979).

Many elements exist in several isotopic forms in nature. The mass selective detector will also show peaks which correspond to the same molecule but with heavier isotopes. The ratio of the intensity of the molecular ion peak to the intensities of the peaks corresponding to the heavier isotopes is determined by the natural abundance of each isotope. Because each type of molecule has a unique combination of atoms, and because each type of atom and its isotopes exist in a unique ratio in nature, the ratio of the intensity of the molecular ion peak to the intensities of the isotopic peaks can provide information about the numbers of each type of atom present in the molecule. Thus, isotope ratio spectrometry can be used to determine the molecular formula of a substance and aid in positive identification (Pavia *et al.*, 1979).

An overlay of a chromatogram for chloroform showing the mass 83 and 85 peaks is provided in the following figure. The ratios of these peaks are 1:  $\frac{2}{3}$  according the corresponding ratio of chlorine isotopes (mass 35 and 37). This

ratio (1: 3) was used to verify identification of chloroform in each sample tested on the GC/MS used in this study.

The mass spectrum of a compound has been shown to be like a fingerprint that can be used to identify the original structure. By matching the retention time and mass spectrum as well as isotopic ratios of an unknown substance with those of a standard compound analyzed using the same GC/MS conditions, positive identification can be obtained.

The technique of selected ion monitoring (SIM) is used in target compound determinations. In a SIM analysis, only a few characteristic mass-to-charge ratios of each analyte are monitored instead of scanning the mass analyzer across the entire mass range. The advantage of this approach is an improvement in signal to noise ratio for the few masses monitored, allowing a reduction in detection limits by a factor of approximately 100 (Clement (1989)).

Compounds in complex samples, such as wastewater, are best quantified using the SIM technique. Quantification is performed by comparing the response of a peak with the response of either an internal or external standard of a substance that may be in a related compound class.

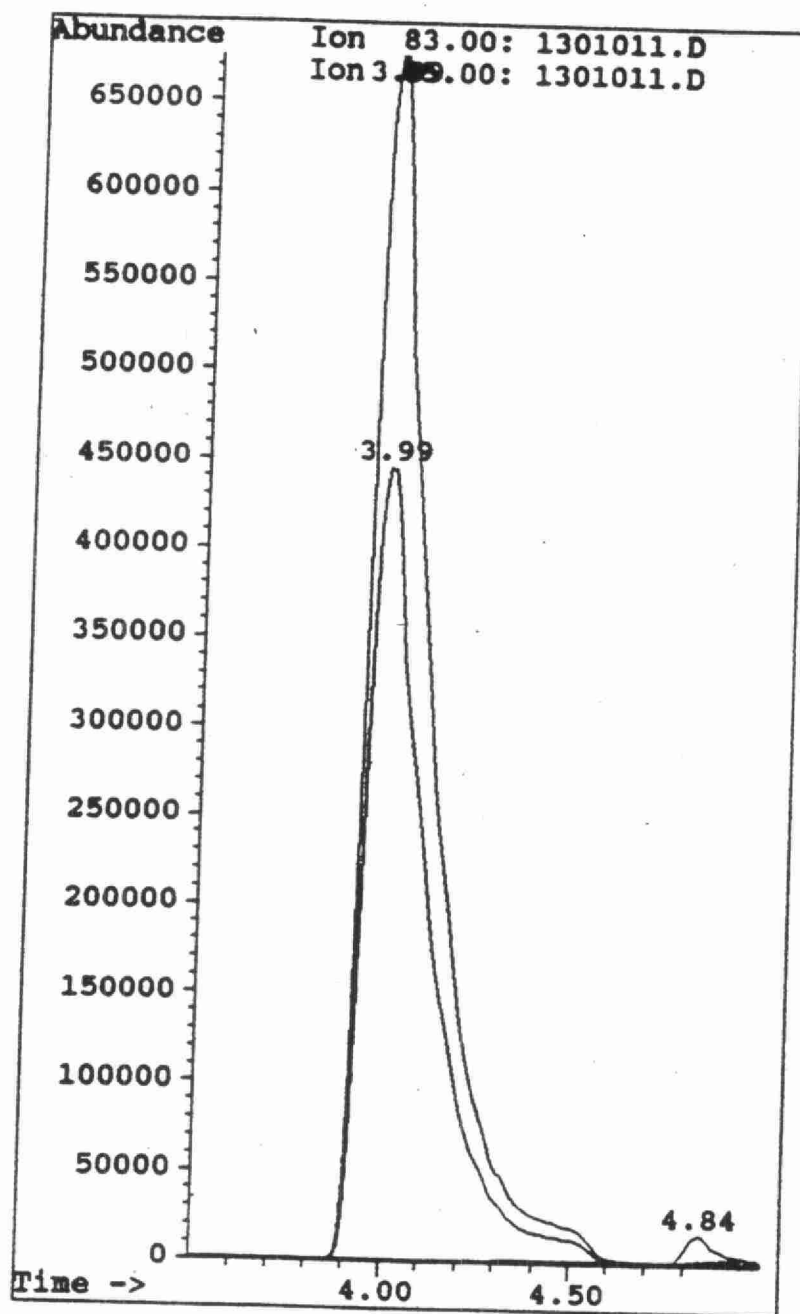
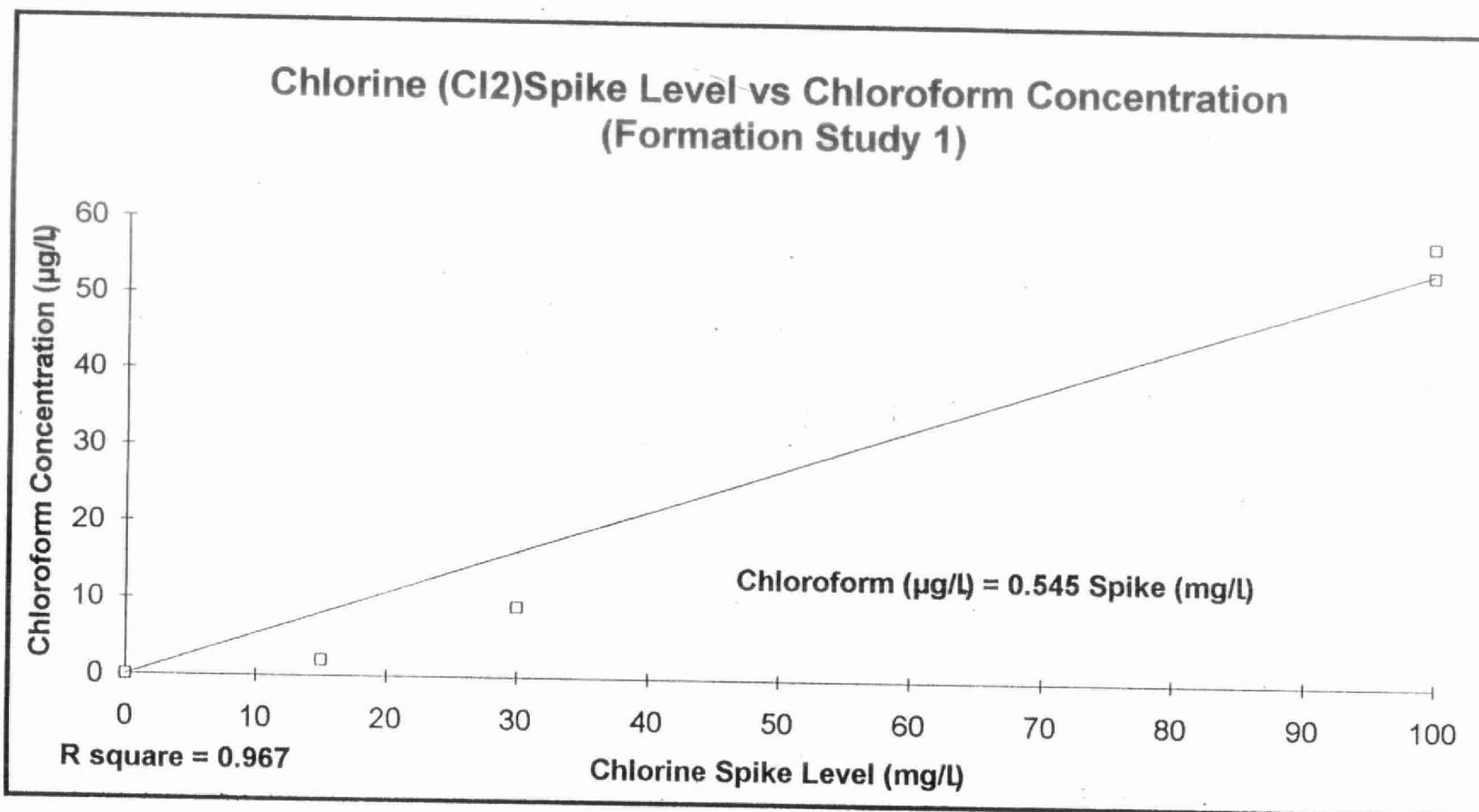
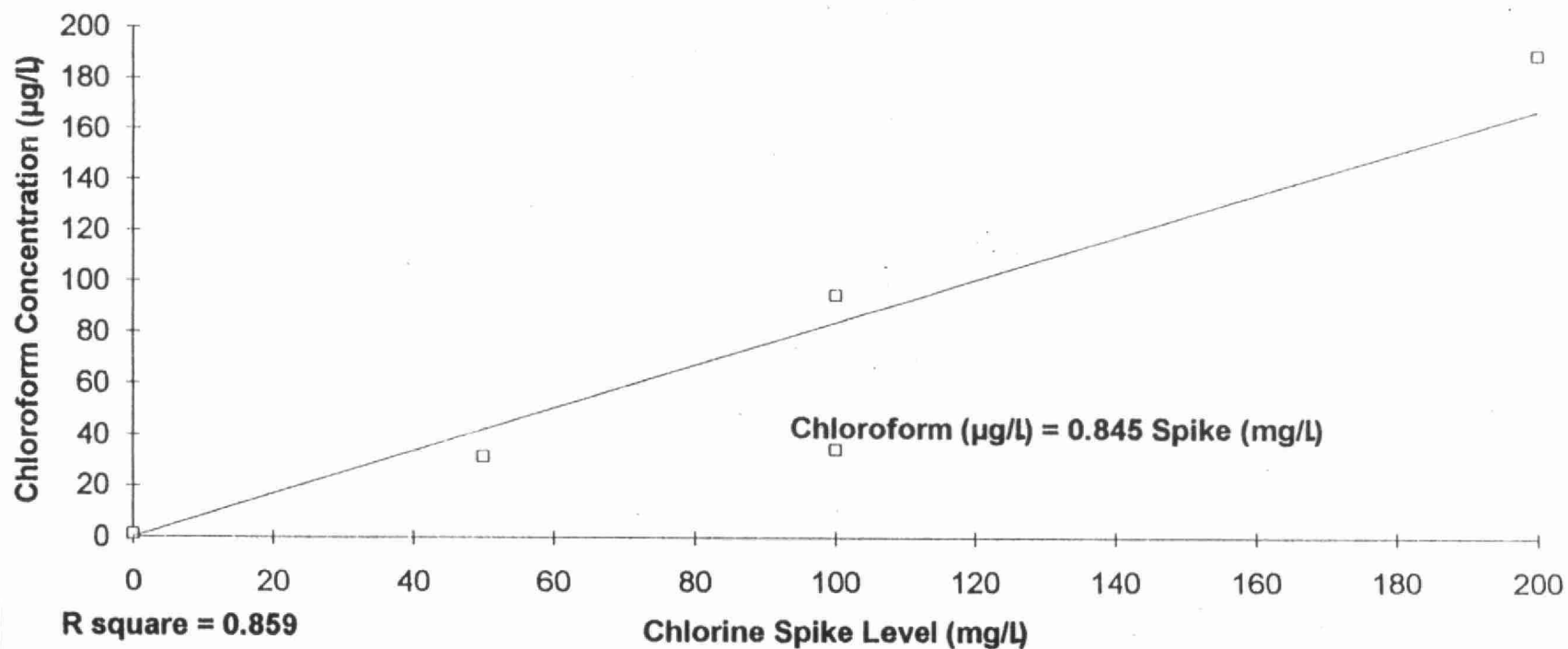


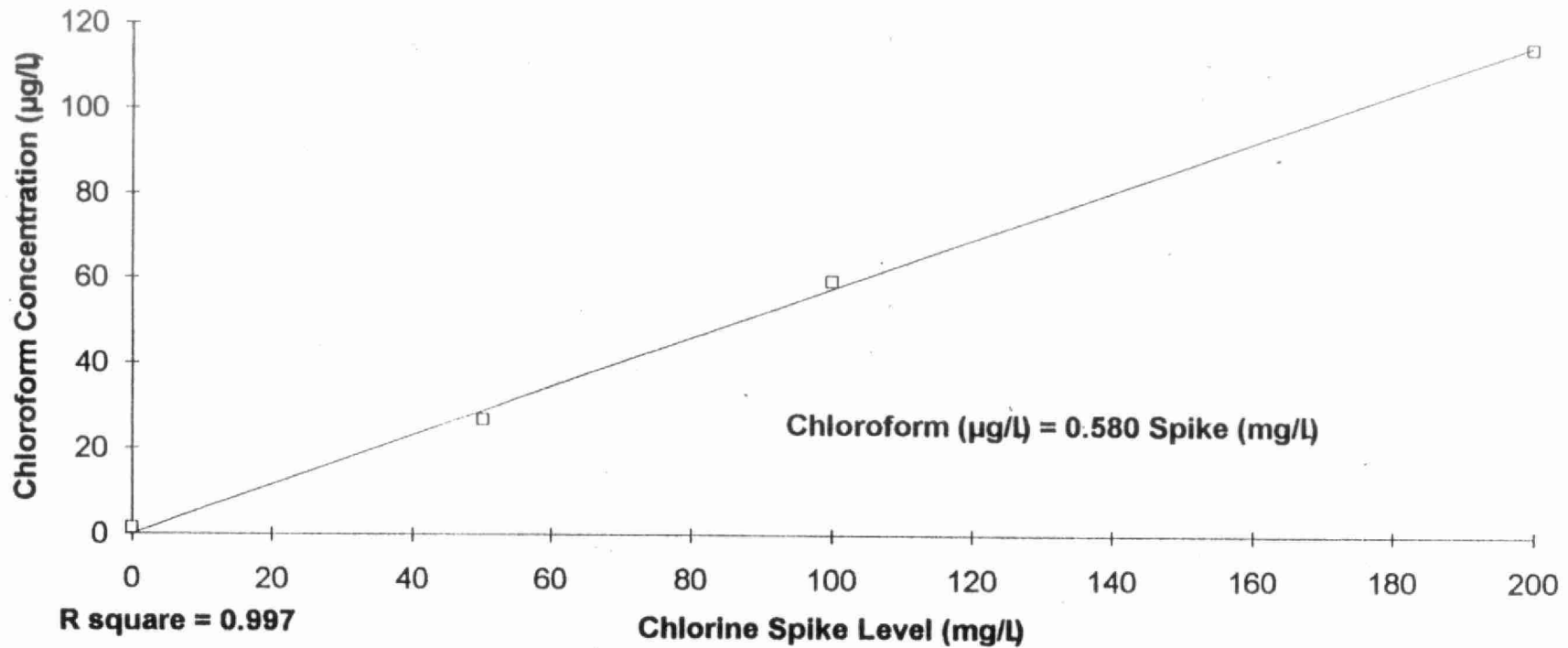
Figure Overlay of 83,85 peaks



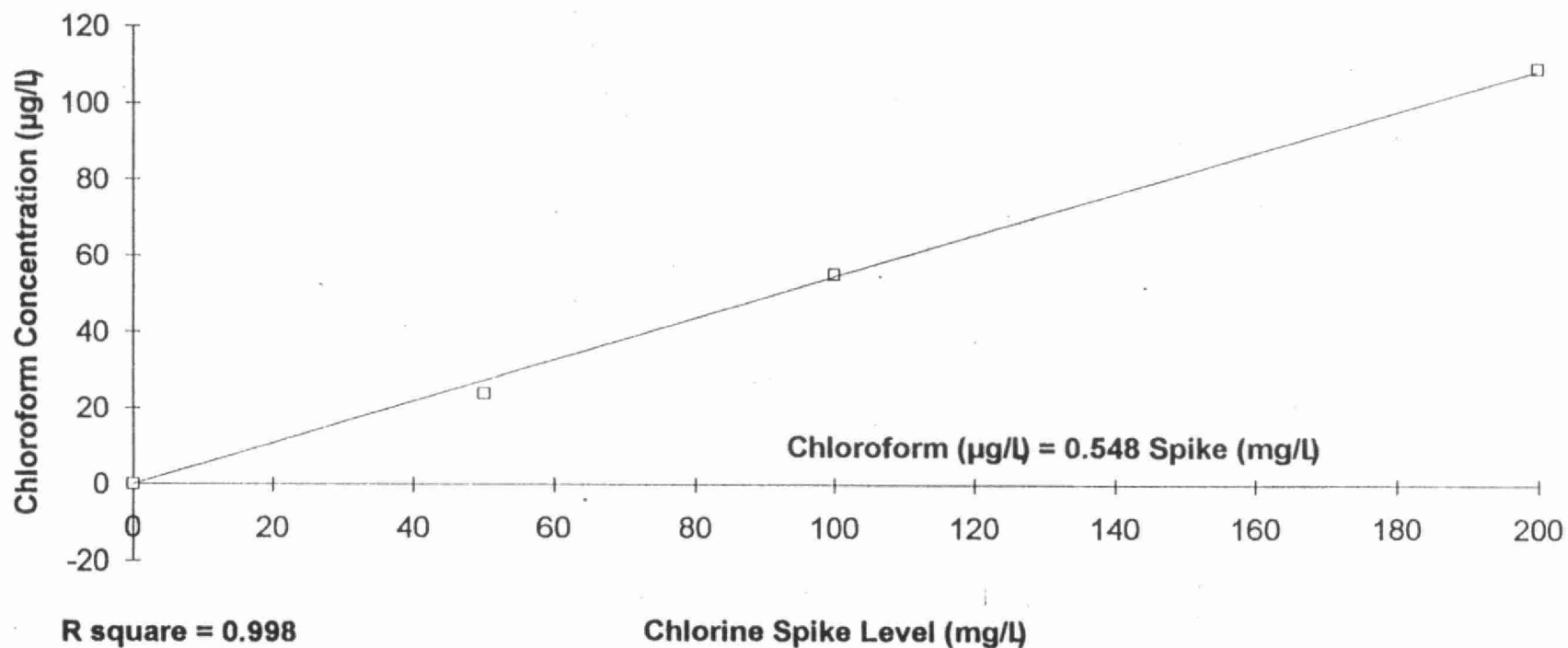
### Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 2)



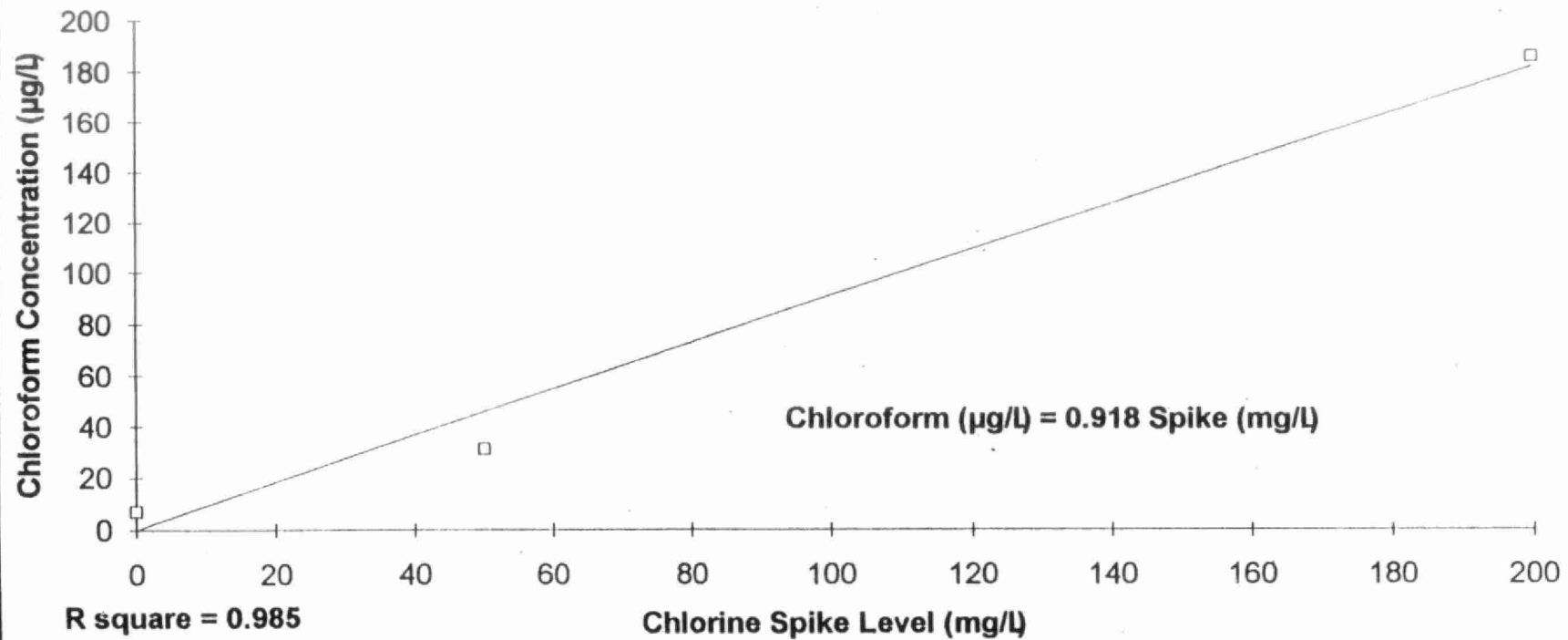
### Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 3)



### Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 4)

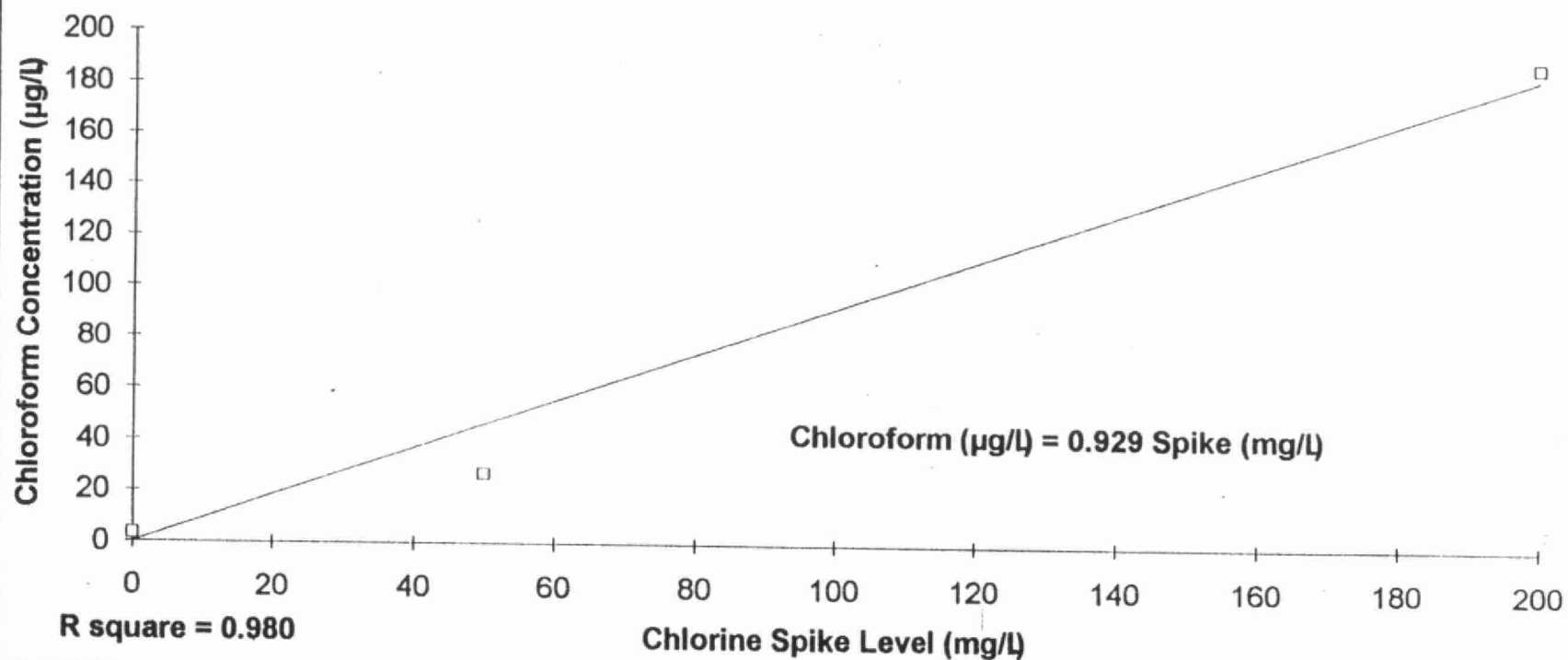


### Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 5)

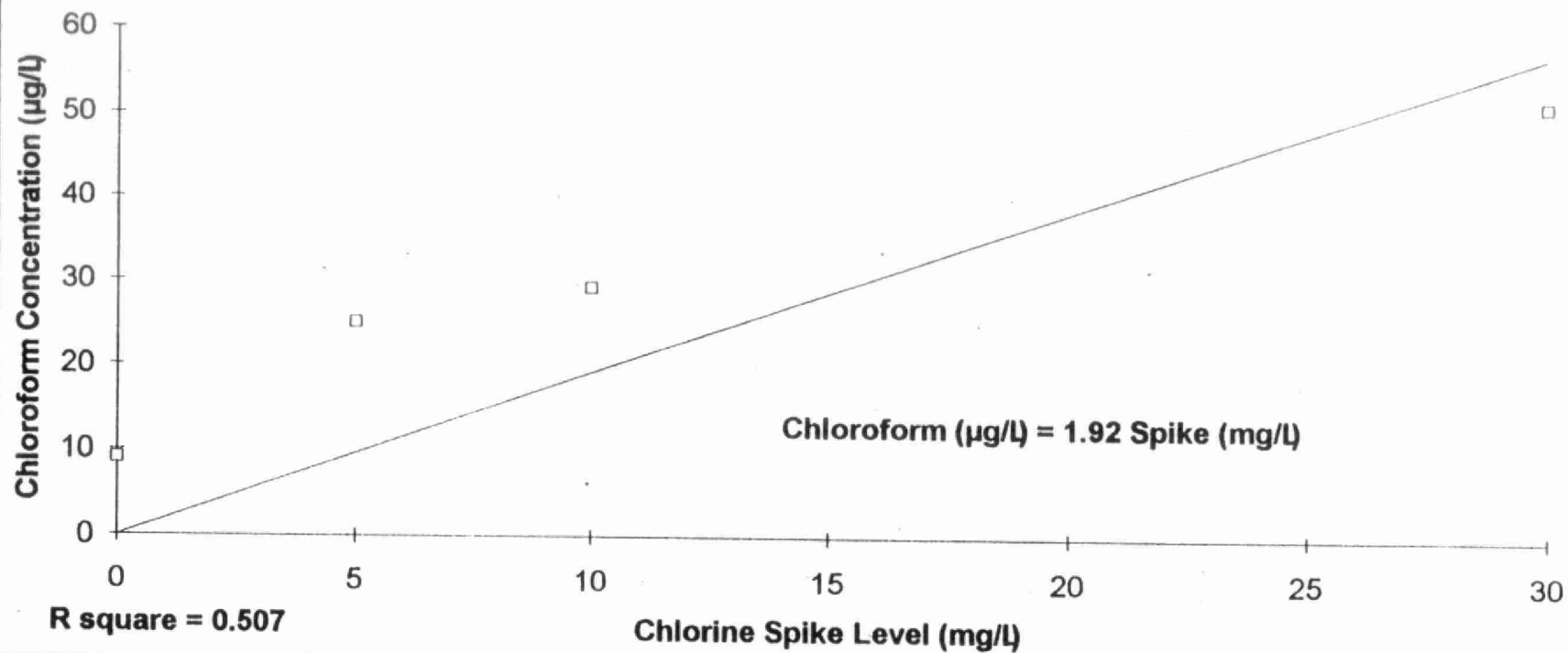




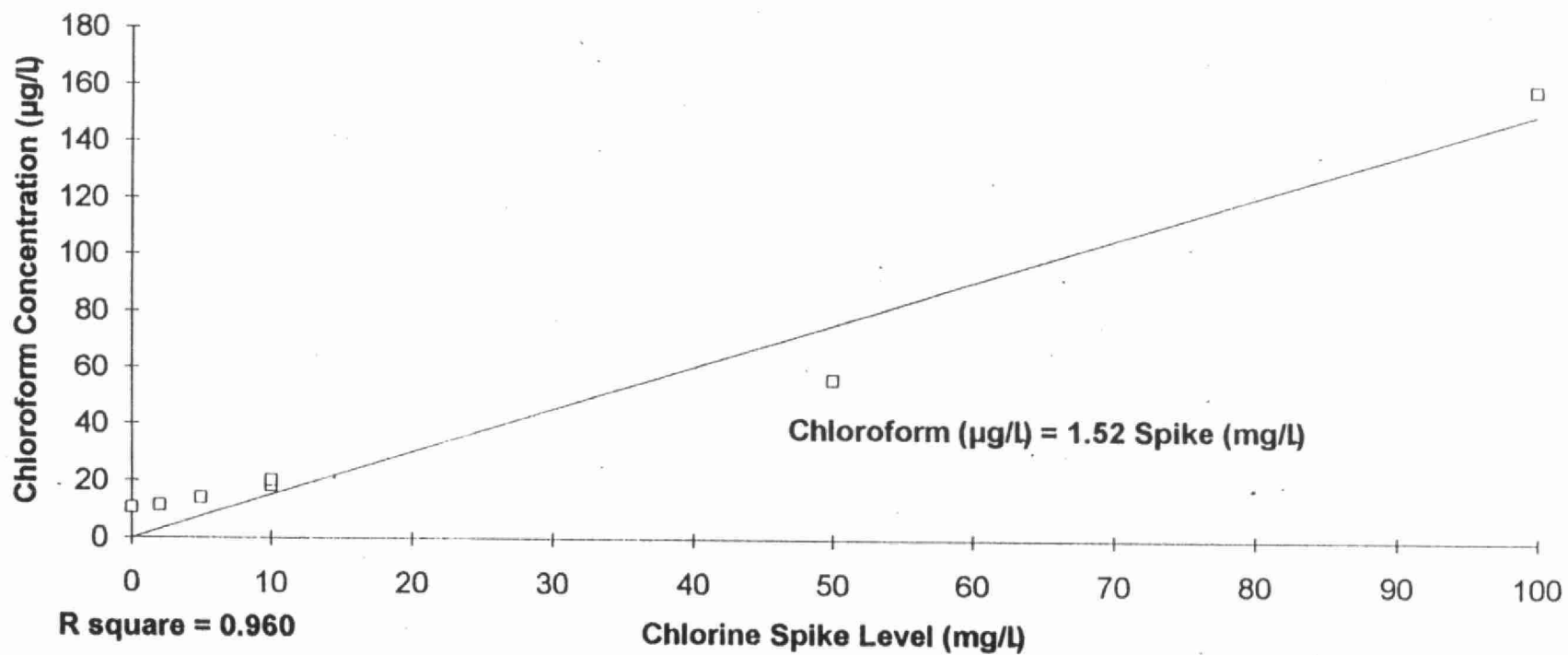
# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 6)



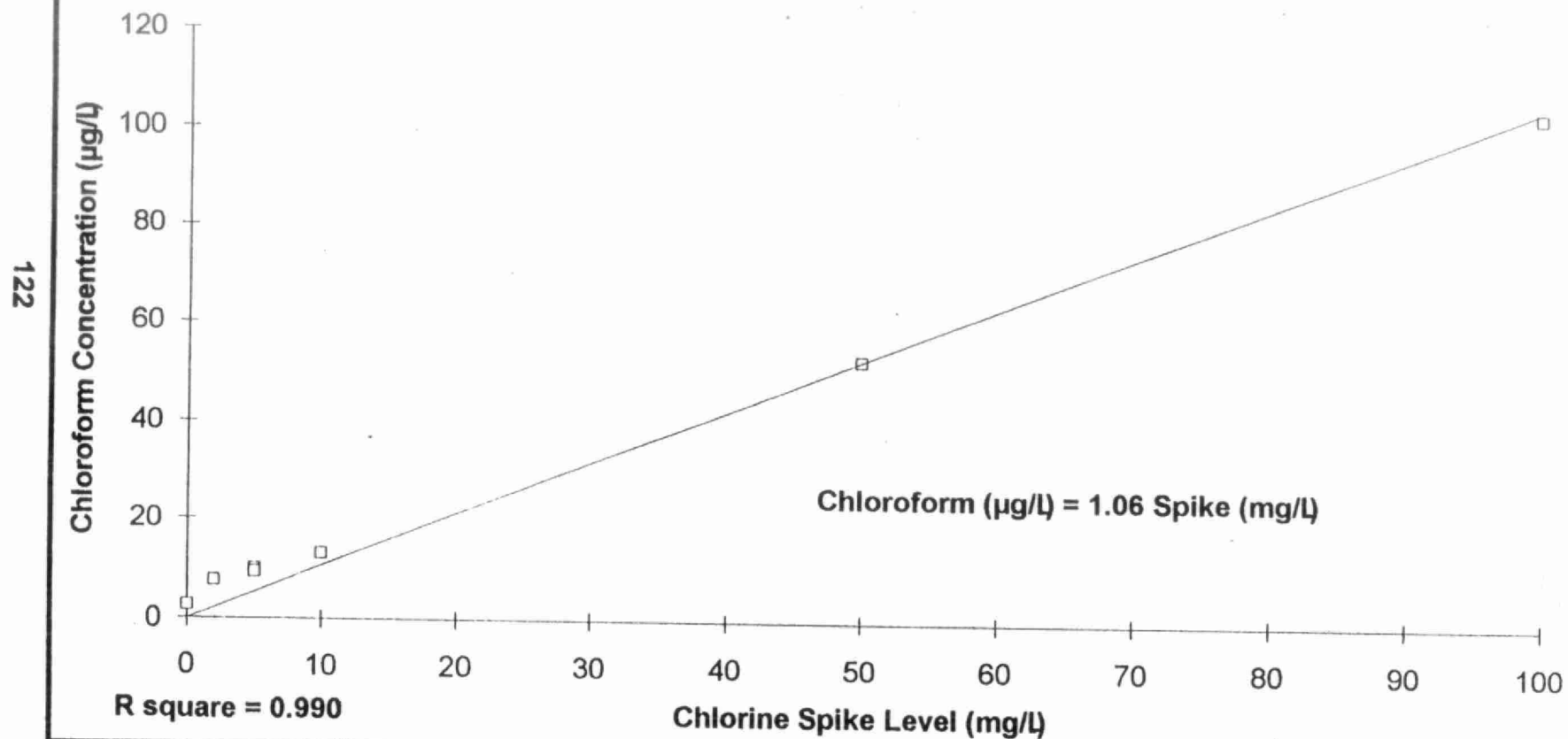
# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 7)



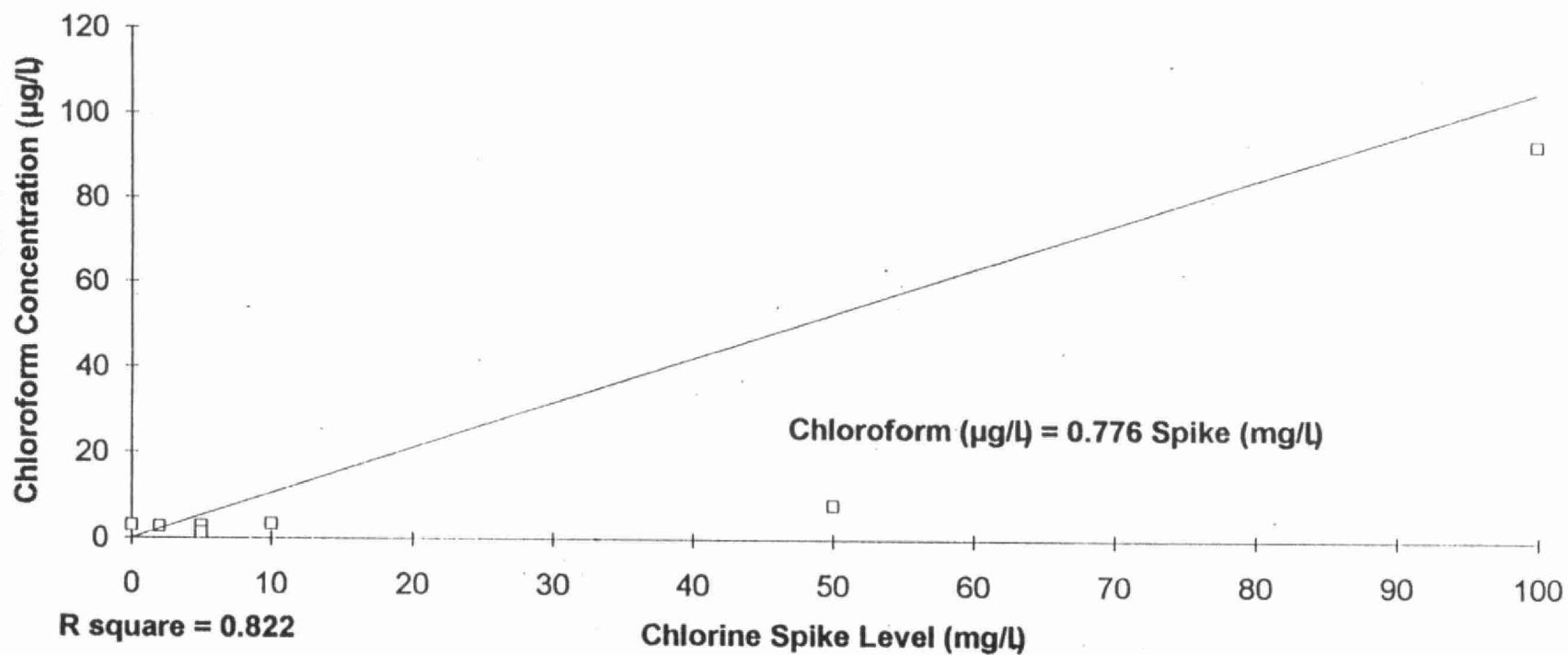
### Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 8)



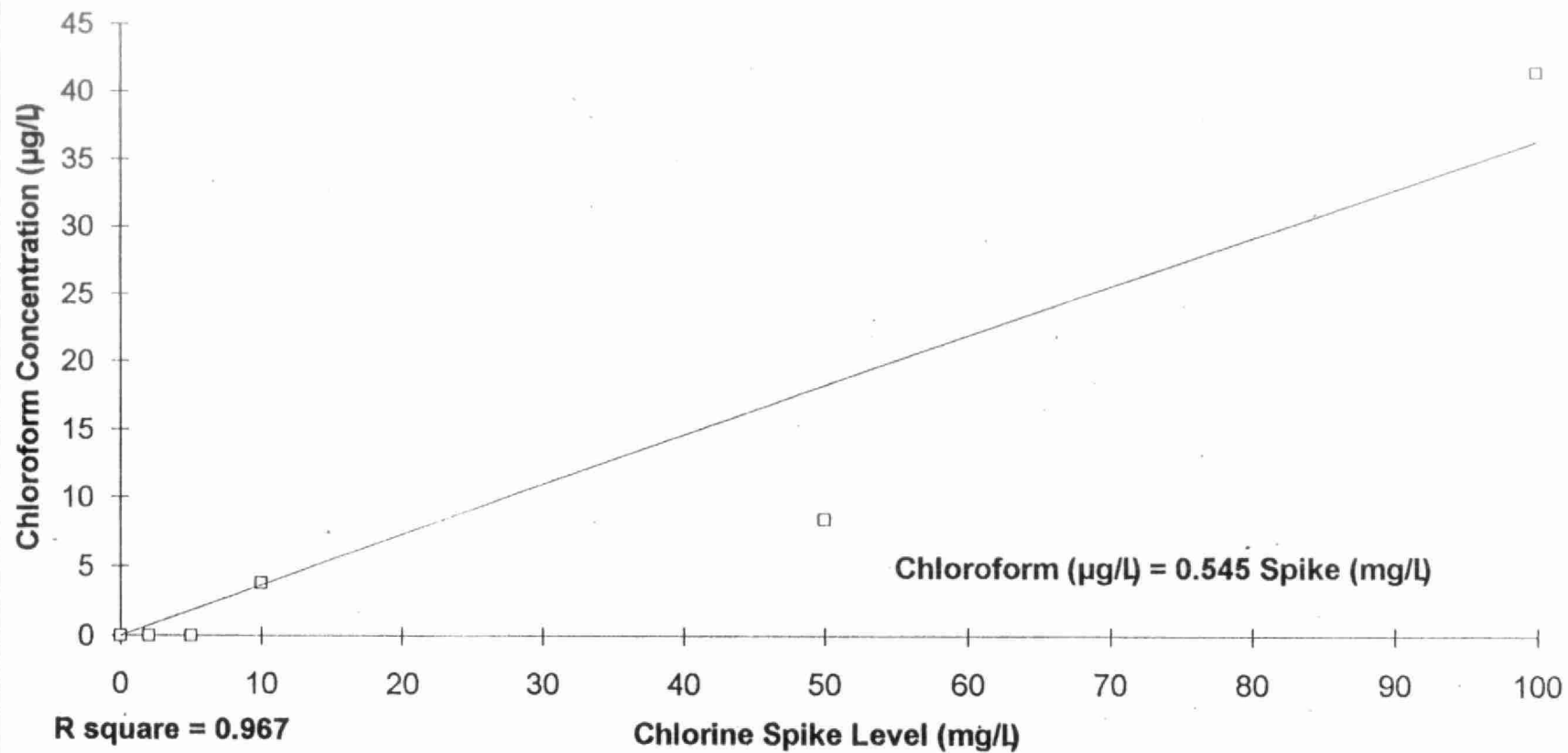
# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 9)



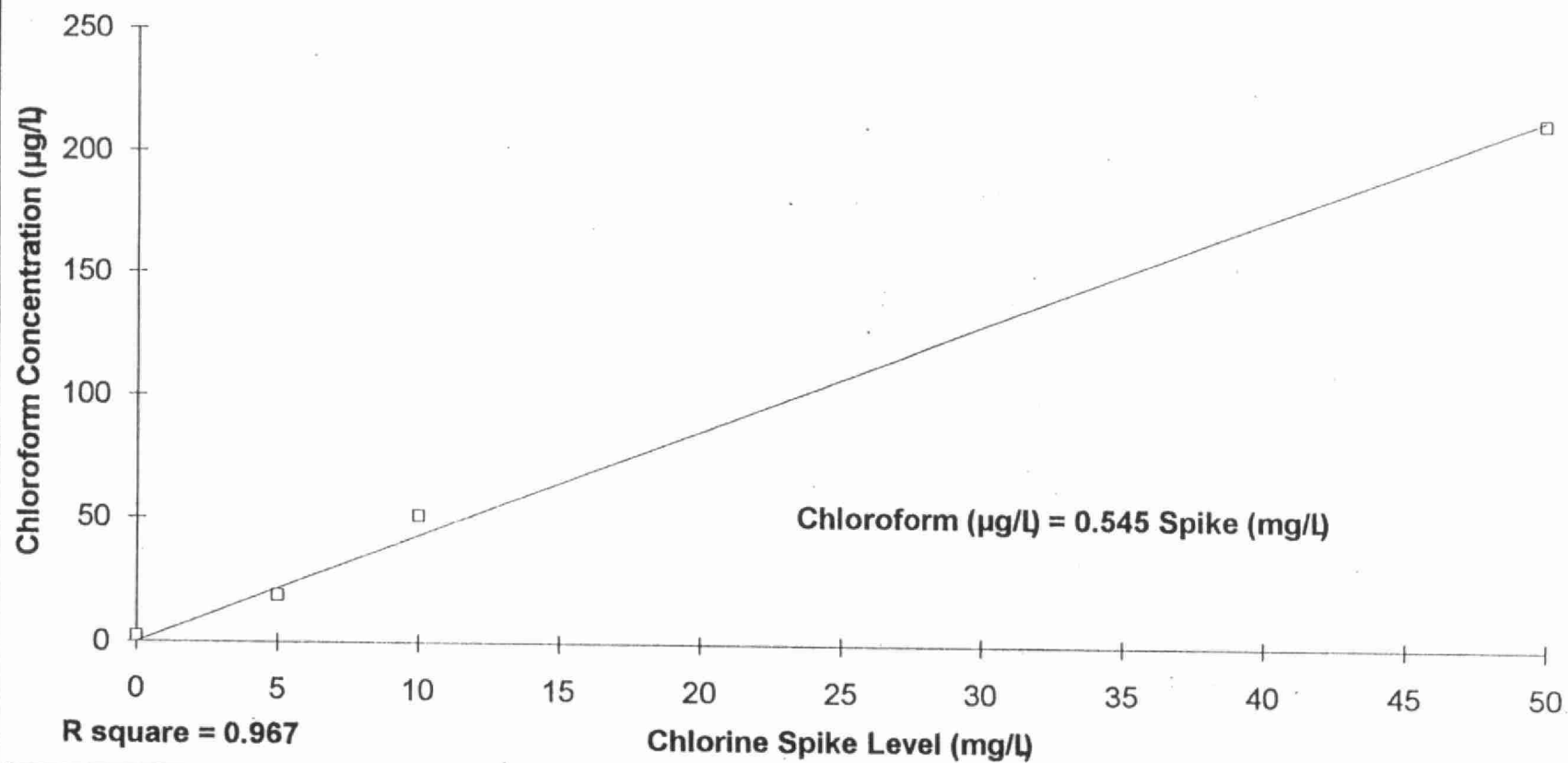
### Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 10)



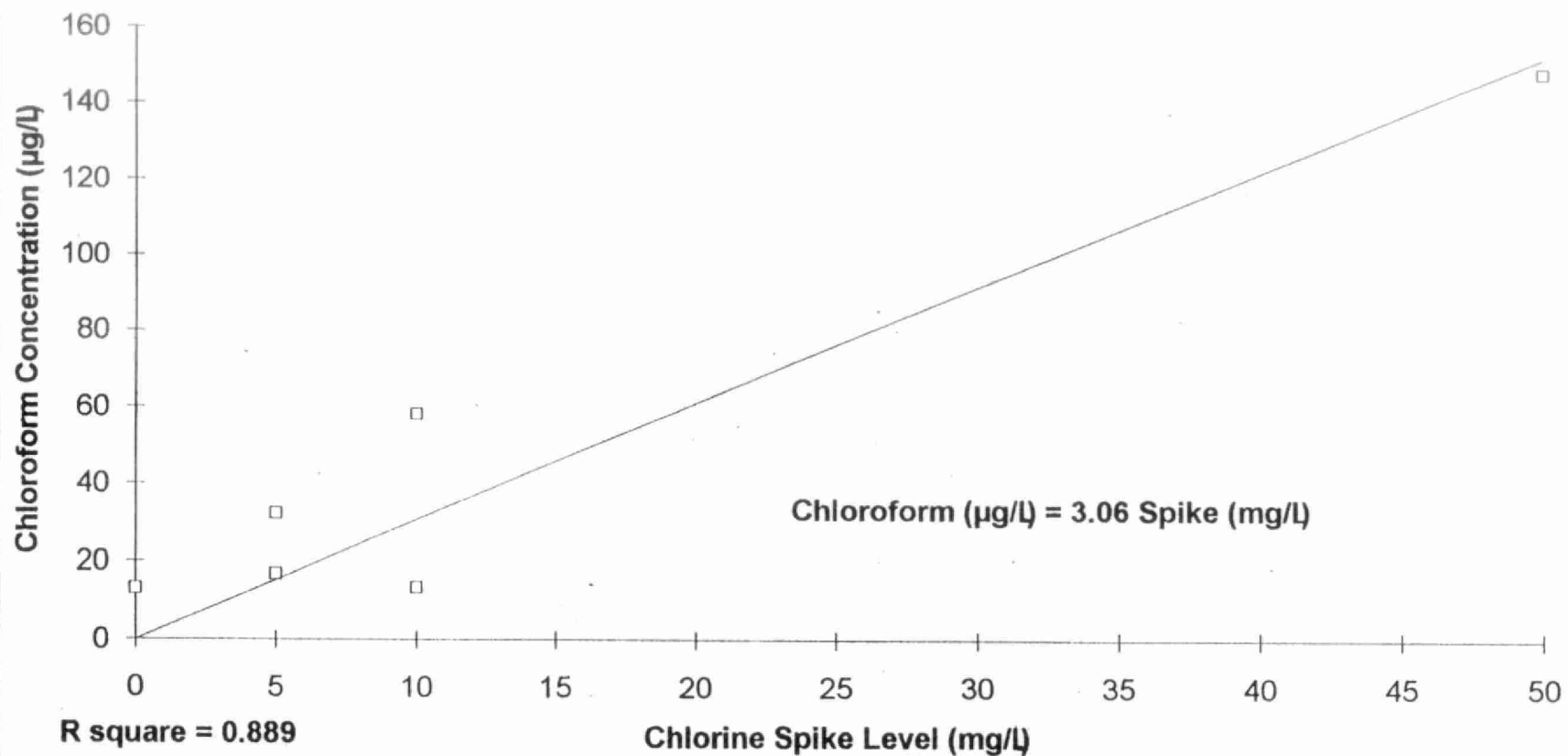
# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 11)



# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 12)

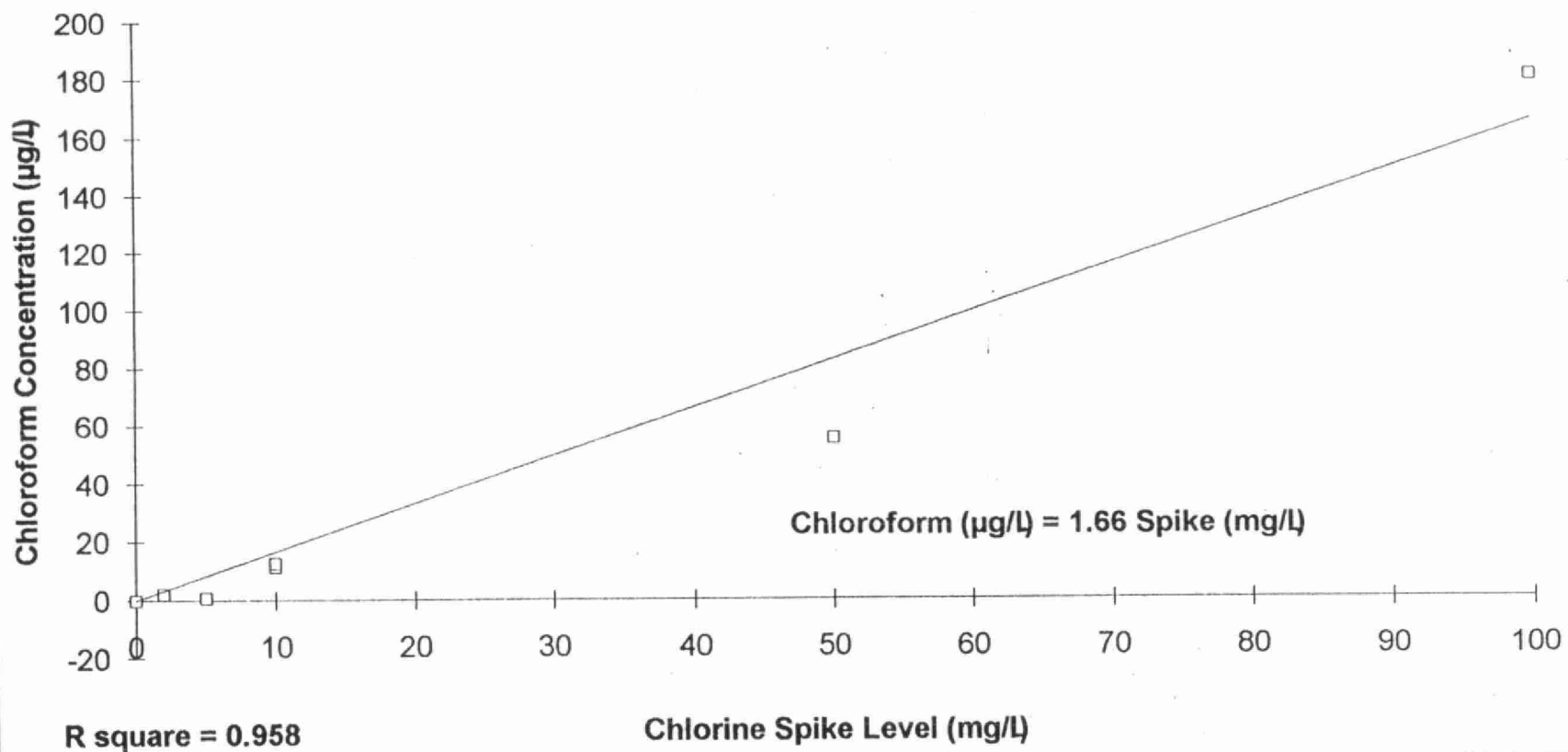


# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 13)

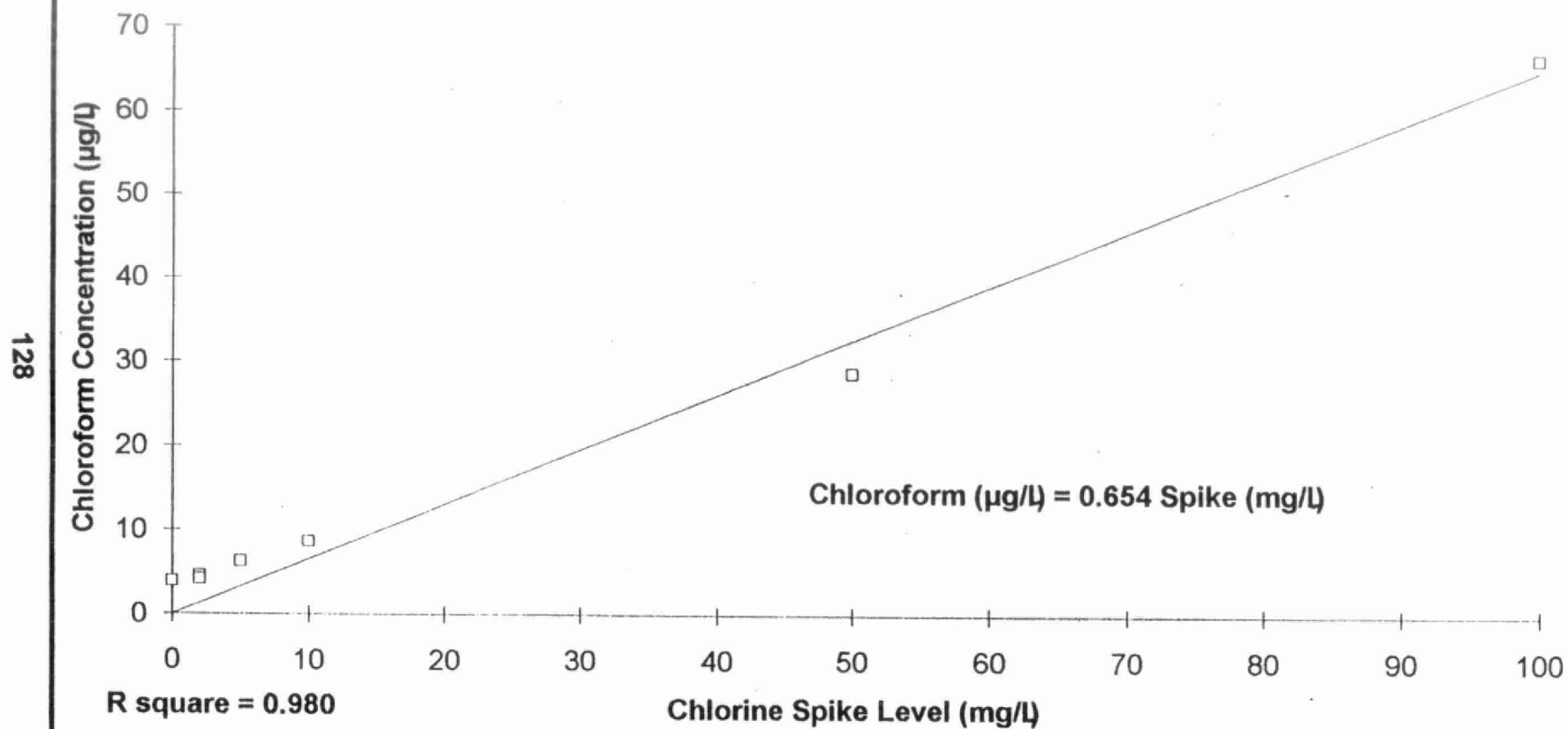




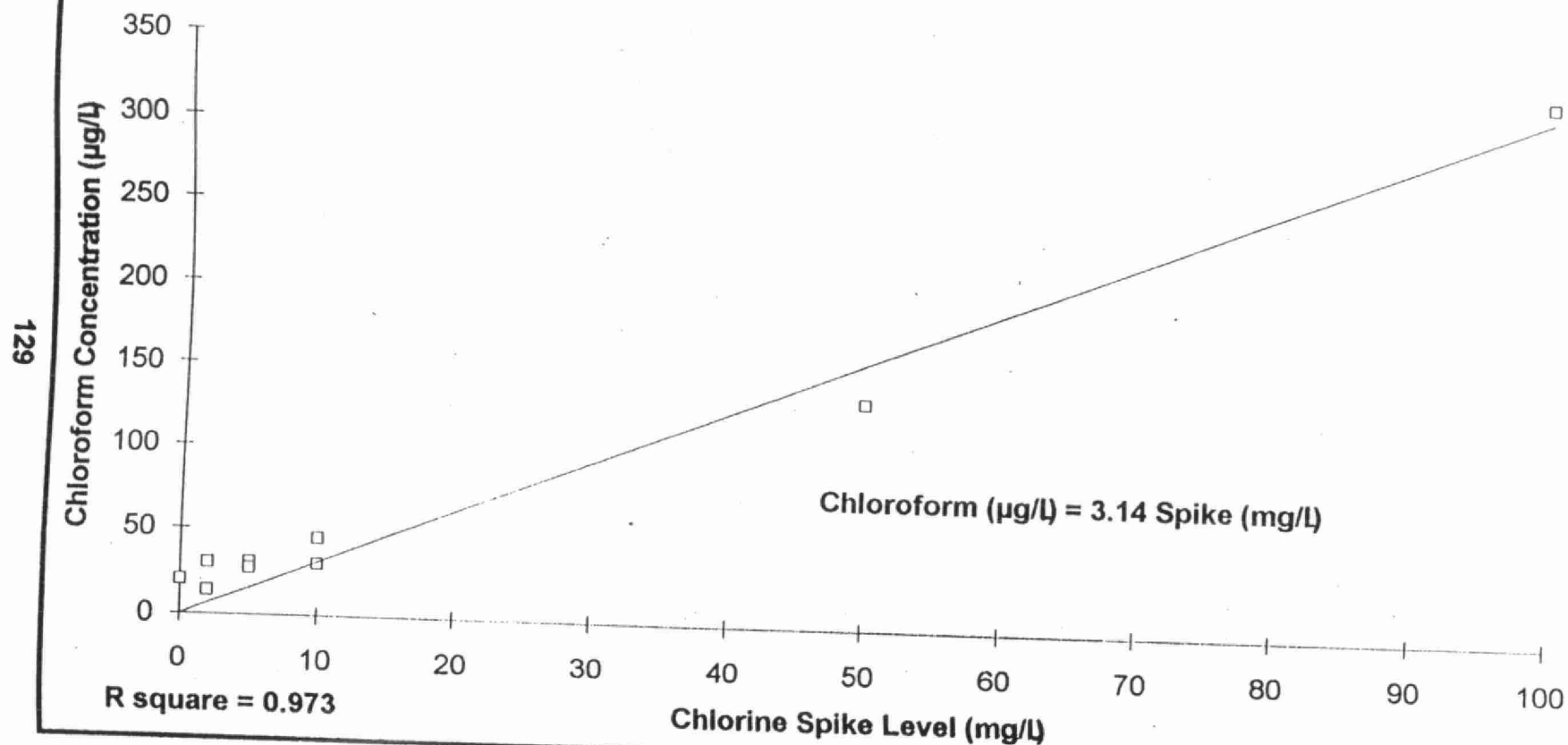
# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 14)



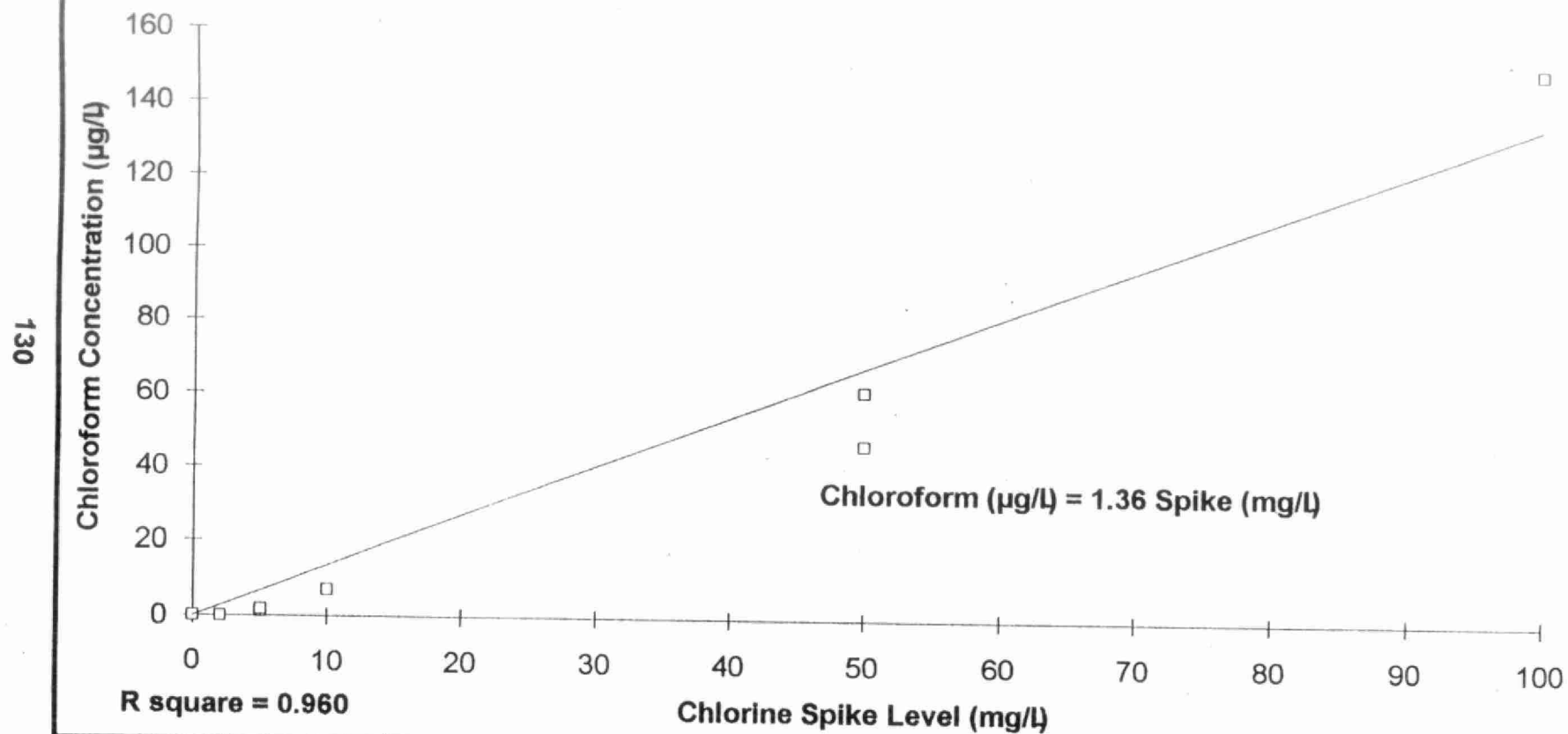
# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 15)



# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 16)



# Chlorine (Cl<sub>2</sub>) Spike Level vs Chloroform Concentration (Formation Study 17)



## 7. INTEGRATED FATE MODEL

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At the present time only one commercial computer-based fate model (*CORAL+*) is available for predicting VOC emissions from sewers. The *CORAL+* model simulates a single sewer reach with the option of a single drop structure at the downstream end of the reach. The *CORAL+* model serves as the computational "backbone" for a multi-reach network model developed as part of this study. A technical description of, and user documentation for, the multi-reach model is provided as Volume VIII (Model Documentation). The remainder of this chapter provides an overview of the *CORAL+* backbone.

The *CORAL+* model is an enhanced version of *CORAL* (Collection system Organic Release ALgorithm), the latter having been developed and published in 1989 by Dr. Richard L. Corsi. The model predicts VOC emissions from gravity-flow sewers based on a simultaneous solution of mass balance equations for both the aqueous phase (wastewater) and gas phase (sewer headspace).

The *CORAL+* model uses mass transfer equations which were described in Chapter 4 of this report. In particular, Equations 4-1 through 4-4 are used for estimating gas-liquid mass transfer along sewer reaches. Gas-phase resistance to mass transfer is estimated by using a constant ratio of  $k_g/k_l = 100$ . Emissions from drop structures are based on a model relating oxygen and VOC mass transfer coefficients, with an adjustment for enhanced gas-phase resistance associated with entrained air bubbles. Models and pilot experiments used for model evaluation are described in detail in the papers comprising Volume V.

The *CORAL+* model, and subsequent multi-reach model, contains a data base of physicochemical properties of over 40 common VOCs. Both steady-state and dynamic models are included as well as a sensitivity analysis feature. The latter can be used to assess the effects of several variables/parameters (pipe diameter, wastewater flowrate, channel slope, headspace ventilation rate, etc.) on VOC emissions.

Applications of the *CORAL+* model are described in Chapter 4 of this report. Although the *CORAL+* model, and multi-reach model, are unique, they do have a limitation in terms of requiring users to input headspace ventilation rates. There is currently a paucity of information related to natural ventilation of sewers. Ventilation rates presented in Chapter 3 of this report, i.e., for the Massey Creek Interceptor, can be assumed to be relatively high for most municipal sewers. Research is currently underway by Enviromega Ltd and The University of Texas at Austin to improve the existing knowledge-base associated with natural ventilation of sewers. When completed, results of these studies should facilitate the use of existing fate models for sewers.

# **Fate of Volatile Organic Compounds in Wastewater Collection Systems**

**Volume VIII: Model Documentation**

Enviromega Ltd.

under the supervision of John Bell (co-investigator)

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

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# DERIVATION OF MODELS IN *TOXCHEM*+

The *TOXCHEM* model incorporates a number of fate mechanisms for toxic contaminants into process-specific mass balance equations. In the following sections the relationships defining the individual fate and transport mechanisms are initially presented. The process specific mass balance equations are presented subsequently.

## 1. Fate and Transport Mechanisms

### 1.1 Liquid-Gas Mass Transfer

Volatile contaminants may be removed from wastewater by volatilization into the atmosphere. Volatilization of contaminants to the atmosphere may occur wherever air-water interfaces exist, such as from the surface of open tanks and process vessels or in aeration processes.

#### 1.1.1 Volatilization from Surfaces

The rate of volatilization from the surface of a process vessel is given by,

$$r_v = K_L a (C - C^*) V \quad (1)$$

where,

- $r_v$  = rate of volatilization, mg/h,
- $K_L$  = overall mass transfer coefficient, m/h,
- $a$  = specific interfacial area for mass transfer,  $m^2/m^3$ ,
- $C$  = concentration of volatile compound in the water,  $mg/m^3$ ,
- $C^*$  = equilibrium concentration of compound in water,  $mg/m^3$ .
- $V$  = volume of process vessel,  $m^3$ .

The specific interfacial area for surface volatilization is taken to be the liquid surface area divided by the tank volume.

For low contaminant concentrations, equilibrium between the liquid and gas phases can be represented by Henry's law:

$$C_g = H C^* \quad (2)$$

where,

- $H$  = Henry's law coefficient,  $m^3 \text{ liquid}/m^3 \text{ gas}$ .

Combining Equations 1 and 2 yields:

$$r_v = k_v \left( C - \frac{C_g}{H} \right) V \quad (3)$$



where,

$$k_v = K_L a = \text{volatilization rate constant, h}^{-1}.$$

For a system open to the atmosphere, it is assumed that the air movement above the basin is sufficient to carry the volatilized compounds away so that their bulk concentration in the air phase is negligible. In that case the equilibrium water phase concentration will also be negligible. Therefore Equation 3 becomes,

$$r_v = k_v C V \quad (4)$$

The mass transfer coefficients for surface volatilization can be estimated using the following correlations developed by Mackay and Yeun (1983):

$$k_G = 10^{-3} + 46.2 \times 10^{-3} U^* Sc_G^{-0.67} \quad (5)$$

$$k_L = 10^{-6} + 34.1 \times 10^{-4} U^* Sc_L^{-0.5} \quad (U^* > 0.3) \quad (6)$$

$$k_L = 10^{-6} + 144 \times 10^{-4} U^{*2.2} Sc_L^{-0.5} \quad (U^* < 0.3) \quad (7)$$

$$U^* = 10^{-2} (6.1 + 0.63 U_{10})^{0.5} U_{10} \quad (8)$$

where,

- $k_G$  = gas film mass transfer coefficient, m/s,
- $k_L$  = liquid film mass transfer coefficient, m/s,
- $U^*$  = air side friction velocity, m/s,
- $U_{10}$  = wind velocity 10 m above the water surface, m/s,
- $Sc_G$  = gas phase Schmidt number, dimensionless,
- $Sc_L$  = liquid phase Schmidt number, dimensionless.

The Schmidt numbers are calculated as follows:

$$Sc_G = \frac{\nu_s}{D_G d_s} \quad (9)$$

$$\nu_s = 1.8 \times 10^{-4} \quad (10)$$

$$D_G = 0.0067 T^{1.5} \frac{\left[ 0.034 + \frac{1}{M} \right]^{0.5}}{M^{0.17} \left\{ \left[ \frac{M}{2.5 d_c} \right]^{0.33} + 1.81 \right\}^2} \quad (11)$$

$$d_s = 1.2928 \times 10^{-3} \frac{273.16 (760 - 0.08694h)}{T \cdot 760} \quad (12)$$

$$Sc_L = \frac{v_w}{D_L d_w} \quad (13)$$

$$v_w = \frac{1}{2.1482 [ (T_c - 8.435) + [ 8078.4 + (T_c - 8.435)^2 ]^{0.5} ] - 120.0} \quad (14)$$

$$D_L = 5.06 \times 10^{-9} \frac{T d_c^{0.6}}{M^{0.6} v_w} \quad (15)$$

$$d_w = 0.9982 \quad (16)$$

where,

- $d_c$  = density of compound, g/cm<sup>3</sup>,
- $d_a$  = density of air, g/cm<sup>3</sup>,
- $d_w$  = density of water, g/cm<sup>3</sup>,
- $v_a$  = viscosity of air, g/cm•s,
- $v_w$  = viscosity of water, g/cm•s,
- $D_G$  = diffusion coefficient of compound in air, cm<sup>2</sup>/s,
- $D_L$  = diffusion coefficient of compound in water, cm<sup>2</sup>/s,
- $h$  = elevation above sea level, m,
- $T$  = temperature, °K,
- $T_c$  = temperature, °C,
- $M$  = molecular weight of compound, g/mol.

The overall mass transfer coefficient can be obtained from the liquid film and gas film mass transfer coefficients based on two-film theory (Lewis and Whitman, 1924). The overall mass transfer coefficient is calculated as follows:

$$K_L = \left\{ \frac{1}{k_L} + \frac{1}{Hk_G} \right\}^{-1} \quad (17)$$

where,

- $K_L$  = overall mass transfer coefficient, m/h,
- $k_L$  = gas film mass transfer coefficient, m/h,
- $k_G$  = liquid film mass transfer coefficient, m/h.

### 1.1.2 Air Stripping

#### *Mechanical Aeration*

Process vessels may be aerated by either submerged diffusers or mechanical surface aerators. The equation describing the contaminant removal rate by stripping for mechanical aeration is similar to Equation 1 or Equation 3,

$$r_s = K_L a (C - C^*) V = k_s (C - \frac{C_g}{H}) V \quad (18)$$

where,

- $r_s$  = stripping rate, mg/h,
- $k_s$  =  $K_L a$  = stripping rate constant,  $h^{-1}$ .

For mechanical aeration systems open to the atmosphere, the equilibrium concentration,  $C^*$ , is assumed to be zero since the atmosphere around the aerator is considered to be free of the volatilizing compound. Equation 18 can then be rewritten as,

$$r_s = k_s C V \quad (19)$$

The overall mass transfer coefficient can be obtained from the liquid film and gas film mass transfer coefficients (Equation 17).

The liquid film mass transfer coefficient for surface aeration can be related to the oxygen transfer coefficient, assuming that oxygen mass transfer is liquid phase controlled,

$$k_L = K_L^{oxy} \left[ \frac{D_c}{D_{oxy}} \right]^n = K_L^{oxy} \psi \quad (20)$$

where,

$$\psi = \left[ \frac{D_c}{D_{oxy}} \right]^n \quad (21)$$

and,

- $K_L^{oxy}$  = oxygen transfer coefficient, m/h,
- $D_c$  = diffusion coefficient of compound in water,  $cm^2/s$ ,
- $D_{oxy}$  = diffusion coefficient of oxygen in water,  $cm^2/s$ ,
- $n$  = proportionality parameter between 0.5 and 1.0, dimensionless.

Combining Equation 20 with a correlation for the oxygen transfer rate constant, the following equation, proposed by Thibodeaux (1979), is used to estimate the liquid phase mass transfer coefficient for mechanical surface aeration:

$$k_L a = 109.39 N_{oxy} E P \alpha (1.024)^{(T-20)} \left[ \frac{D_c}{D_{oxy}} \right]^{0.5} \left[ \frac{1}{V} \right] \quad (22)$$

where,

- $N_{oxy}$  = standard oxygen transfer rate for aerator,  $kg/kW \cdot h$ ,
- $E$  = power delivery efficiency for aerator, dimensionless,
- $\alpha$  = dirty water/clean water conversion factor, dimensionless,
- $P$  = aerator power,  $kW$ ,
- $T$  = temperature,  $^{\circ}C$ ,
- $V$  = volume of aeration basin,  $m^3$ .

To determine the overall mass transfer coefficient, the gas phase mass transfer coefficient must be estimated. Equation 17 can be rewritten as

$$K_L a = k_L a \frac{\frac{k_G H}{k_L}}{\frac{k_G H}{k_L} + 1} \quad (23)$$

Munz and Roberts (1989) suggest a value of 40 for the ratio of the gas and liquid film mass transfer coefficients, i.e.,

$$\frac{k_G}{k_L} = 40 \quad (24)$$

Combining Equations 23 and 24 yields,

$$K_L a = k_L a \frac{40H}{40H + 1} \quad (25)$$

### Diffused Bubble Aeration

For diffused bubble aeration, the rate of stripping is equal to the contaminant concentration in the air bubbles times the air flow rate:

$$r_s = Q_a C_g \quad (26)$$

where,

$$\begin{aligned} r_s &= \text{stripping rate, mg/h,} \\ Q_a &= \text{air flow rate, m}^3/\text{h,} \\ C_g &= \text{contaminant concentration in air bubbles, mg/m}^3. \end{aligned}$$

Equation 26 can be rewritten in terms of the contaminant concentration in the wastewater:

$$r_s = Q_a f H C = k_s C V \quad (27)$$

where,

$$\begin{aligned} f &= \text{fractional saturation of gas bubbles, dimensionless.} \\ k_s &= Q_a f H / V = \text{stripping rate constant, h}^{-1}. \end{aligned}$$

The fractional saturation can be estimated using the following equation proposed by Matter-Muller *et al.* (1981):

$$f = 1 - \exp \left[ \frac{-K_L a V}{Q_a H} \right] \quad (28)$$

For subsurface aeration, the value of  $K_L a$  for the volatile compound can be estimated from Equation 20 using the  $K_L a$  for oxygen under the same conditions. For subsurface aeration, a value of  $n = 0.5$  is used in Equation 20. The overall mass transfer coefficient for the compound is then calculated from Equation 25.

The  $K_L a$  for oxygen for a diffused air system can be related to the oxygen transfer efficiency according to the following equation given by Redmon *et al.* (1983):

$$K_L a_{oxy} = \frac{Q_a d_{oxy} (OTE) Y_{oxy}}{(C_{oxy}^* - C_{oxy}) V} \quad (29)$$

where,

$K_L a_{oxy}$	= oxygen transfer rate constant, $h^{-1}$ ,
$d_{oxy}$	= density of oxygen at mid-depth in basin, mg/L,
OTE	= oxygen transfer efficiency, dimensionless,
$Y_{oxy}$	= mole fraction of oxygen in air, moles of oxygen/mole of air,
$C_{oxy}^*$	= equilibrium oxygen concentration in water at mid-depth, mg/L,
$C_{oxy}$	= oxygen concentration in water at mid-depth, mg/L.

For aerated grit chambers and channels, the oxygen transfer efficiency is generally not known. In the program an OTE value of 0.02 (2%) is assumed for these processes.

### 1.1.3 Volatilization at Weirs

The mass transfer from a falling film can be described by the following differential equation:

$$\frac{dC}{dt} = -K_L a \left( C - \frac{C_g}{H} \right) \quad (30)$$

where,

$t$	= travel time of water from point of spill, h,
$C$	= liquid phase contaminant concentration, mg/m <sup>3</sup> ,
$C_g$	= gas phase contaminant concentration, mg/m <sup>3</sup> ,

If this equation is integrated over the total time for the water to fall from the weir to the receiving trough ( $t_o$ ), the following relationship can be derived:

$$\ln \left\{ \frac{C - \frac{C_g}{H}}{C_o - \frac{C_g}{H}} \right\} = -K_L a t_o \quad (31)$$

where,

$C_o$	= contaminant concentration entering weir, mg/m <sup>3</sup> ,
$C$	= contaminant concentration leaving weir, mg/m <sup>3</sup> .

A similar relationship can be defined for oxygen mass transfer as follows:

$$\ln \left\{ \frac{C_s^{oxy} - C^{oxy}}{C_s^{oxy} - C_o^{oxy}} \right\} = -K_L a_{oxy} t_o \quad (32)$$

where,

$$\begin{aligned} C_s^{oxy} &= \text{oxygen saturation concentration, mg/m}^3, \\ C_o^{oxy} &= \text{oxygen concentration entering weir, mg/m}^3, \\ C^{oxy} &= \text{oxygen concentration leaving weir, mg/m}^3. \end{aligned}$$

Pincince (1991) has defined an empirical relationship between the term on the left of Equation 32 and process variables such as overflow rate and drop height. From Equations 31 and 32 it is apparent that the terms on the left side of the equations are proportional to the mass transfer coefficients. However, the ratio of mass transfer coefficients is related to the ratio of diffusion coefficients:

$$\frac{K_L a}{K_L a_{oxy}} = \left( \frac{D_c}{D_{oxy}} \right) \frac{\frac{k_G H}{k_L}}{\frac{k_G H}{k_L} + 1} \quad (33)$$

Using a ratio of gas phase to liquid phase film coefficients of 100, Equation 33 becomes,

$$\frac{K_L a}{K_L a_{oxy}} = \left( \frac{D_c}{D_{oxy}} \right) \frac{100H}{100H + 1} \quad (34)$$

Therefore, Equations 31, 32 and 34 can be combined to yield:

$$\ln \left\{ \frac{C - \frac{C_g}{H}}{C_o - \frac{C_g}{H}} \right\} = -A \frac{D_c}{D_{oxy}} \left\{ \frac{2H}{2H + 1} \right\} \quad (35)$$

where,

A = empirical relationships defined by Pincince (1991) for primary and secondary clarifiers as follows:

*Primary Clarifier Weirs:*

$$A = 0.042h^{0.872}q^{0.509} \quad (36)$$

*Secondary Clarifier Weirs:*

$$A = 0.077h^{0.623}q^{0.66} \quad (37)$$

where,

$h$  = weir drop height, m,  
 $q$  = weir loading rate,  $\text{m}^3/\text{h}\cdot\text{m}$ .

Equation 35 can be rearranged to solve for the effluent concentration in terms of the influent concentration and the gas concentration:

$$C = (C_o - \frac{C_g}{H}) \exp \left[ -A \frac{D_c}{D_{oxy}} \left( \frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} \quad (38)$$

The mass rate of volatilization from a weir can then be calculated as:

$$r_v = Q (C_o - C) \quad (39)$$

where,

$r_v$  = rate of volatilization from the weir,  $\text{mg}/\text{h}$ ,  
 $Q$  = wastewater flow rate,  $\text{m}^3/\text{h}$ .

#### 1.1.4 Volatilization in Sewer Reaches

Parkhurst and Pomeroy (1972) have published the only model to predict oxygen transfer along sewer reaches. According to their model

$$K_L^{oxy} = 2.67 \times 10^{-4} (1 + 0.17F^2) \gamma (US)^{3/8} \quad (40)$$

where,

$K_L^{oxy}$  = liquid-film mass transfer coefficient,  $\text{m}/\text{s}$ ,  
 $F$  = Froude number  $= U/(gd)^{1/2}$ , dimensionless,  
 $g$  = gravitational acceleration  $= 9.81 \text{ m}/\text{s}^2$ ,  
 $d$  = depth of flow,  $\text{m}$ ,  
 $U$  = wastewater mean velocity,  $\text{m}/\text{s}$ ,  
 $\gamma$  = temperature correction factor, dimensionless,  
 $S$  = slope of the energy grade line,  $\text{m}/\text{m}$ .

The depth of flow ( $d$ ) is obtained by application of Manning's equation. Wastewater mean velocity ( $U$ ) is calculated by dividing wastewater flow rate by wastewater cross-sectional area. The value of  $S$  is assumed to be equal to channel slope, (i.e., uniform flow conditions).

Using the value of  $K_L^{oxy}$  estimated from Equation 40, the liquid mass transfer coefficients for volatile contaminants are obtained from Equation 20, assuming a value of  $n = 0.5$ .



Several researchers have tested and verified the application of Equations 20 and 40 using volatile tracers in sewers with a wide range of operating conditions (Jensen and Hvitved-Jacobsen, 1991; Corsi et al., 1992; Whitmore and Corsi, 1993).

There are currently no published models for estimating values of  $k_g$  in confined sewer environments. In *TOXCHEM+* values of  $k_g$  are estimated using the relationship published by Mackay and Yeun (1983) (Equation 5). For flow through ventilation systems the wind speed is taken to be the gas velocity in the sewer. For uniform ventilation the wind speed is taken to be zero. The overall mass transfer coefficient ( $K_L$ ) is estimated using Equation 17.

### 1.1.5 Volatilization at Drops

Gas-liquid mass transfer at drop structures can occur as a result of three primary mechanisms: 1) transfer to/from the falling film, 2) transfer across an agitated tailwater surface, and 3) transfer to/from air bubbles which become entrained in a drop structure's tailwater pool. Based on computational studies completed by Burnham *et al.*, (1993), gas-liquid mass transfer due to entrained air bubbles is likely to be the dominant transfer mechanism for a wide range of drop structures. Similar assumptions and findings were published by McLachlan *et al.*, (1990) and Nakasone (1986). Thus, *TOXCHEM+* includes an assumption that all contaminant emissions which occur at drop structures are due entirely to air entrainment and associated diffused bubble stripping.

The liquid-phase contaminant concentration downstream of a drop is estimated by relating contaminant to oxygen transfer deficit ratios:

$$r_o = \frac{C_s^{oxy} - C_o^{oxy}}{C_s^{oxy} - C^{oxy}} \quad (41)$$

$$r_v = \frac{C_o - \frac{C_g}{H}}{C - \frac{C_g}{H}} \quad (42)$$

$$r_v = r_o^{\psi_m} \quad (43)$$

where,

- $r_o$  = oxygen deficit ratio, dimensionless,
- $r_v$  = contaminant deficit ratio, dimensionless,
- $C_s^{oxy}$  = saturation dissolved oxygen concentration, mg/m<sup>3</sup>,
- $C_o^{oxy}$  = dissolved oxygen concentration upstream of drop, mg/m<sup>3</sup>,
- $C_o$  = dissolved oxygen concentration downstream of drop, mg/m<sup>3</sup>,
- $C_o$  = contaminant concentration upstream of drop, mg/m<sup>3</sup>,
- $C$  = contaminant concentration downstream of drop, mg/m<sup>3</sup>,
- $C_g$  = contaminant concentration in headspace of drop, mg/m<sup>3</sup>,
- $\Psi_m$  = ratio of contaminant-to-oxygen overall mass transfer coefficients, dimensionless.

The oxygen deficit ratio ( $r_o$ ) is estimated using an empirical model which accounts for variations in drop height, wastewater discharge, and tailwater depth (Nakasone, 1986):

$$\ln r_{o20} = A d^B q^D z^F \quad (44)$$

where,

- $r_{o20}$  = oxygen deficit ratio at 20 °C,
- $d$  = drop height, m,
- $q$  = flow rate per width of stream, m<sup>3</sup>/m•h,
- $z$  = tailwater depth, m.

A, B, D, and F are adjustable parameters obtained from the following table:

d	q	A	B	D	F
≤ 1.2	≤ 235	0.0785	1.31	0.428	3.10
> 1.2	≤ 235	0.0861	0.816	0.428	3.10
≤ 1.2	> 235	5.39	1.31	-0.363	3.10
> 1.2	> 235	5.92	0.816	-0.363	3.10

Estimates of  $r_o$  are adjusted to temperatures other than 20°C using a relationship developed by Gameson *et al.* (1958):

$$\ln r_o = \ln r_{o20} [1 + 0.0168(T - 20)] \quad (45)$$

Combining Equations 42, 43, 44 and 45 yields:

$$\frac{C_o - \frac{C_g}{H}}{C - \frac{C_g}{H}} = [\exp (A d^B q^D z^F [1 + 0.0168 (T - 20)])]^{\Psi_m} \quad (46)$$

The parameter  $\Psi_m$  is related to  $\Psi$  as defined by Equation 21, but accounts for gas-phase resistance to mass transfer, (Hsieh *et al.*, 1992). Since air entrainment is assumed to be the dominant mass transfer mechanism,  $k_G/k_L$  should be representative of diffused aeration systems. Hsieh *et al.* (1992) observed  $k_G/k_L$  ratios ranging from 2.2 to 3.6 for diffused aeration systems. A  $k_G/k_L$  value of 3.0 is used in TOXCHEM+.

$$\psi_m = \frac{\psi}{1 + \frac{1}{H \frac{k_G}{k_L}}} \quad (47)$$

## 1.2 Sorption

Contaminants can be transported from the liquid phase by sorption onto biomass or other solid particles. In a liquid/solid system, at equilibrium, the concentration of a contaminant on a solid sorbent can be expressed by:

$$C_x = K_p C \quad (48)$$

where,

- $C_x$  = concentration of contaminant in solid phase, mg/kg,
- $K_p$  = sorption partition coefficient, m<sup>3</sup>/kg,
- $C$  = concentration of contaminant in liquid phase, mg/m<sup>3</sup>.

Equation 48 is generally valid at low contaminant concentrations.

The sorption partition coefficient for a given compound can be related to the octanol/water partition coefficient of that compound. The following correlation, reported by Dobbs et al. (1989), is used to estimate the sorption partition coefficients where experimentally determined coefficients are not available:

$$\log K_p = 0.58 \log K_{ow} + 1.14 \quad (49)$$

where,

- $K_p$  = sorption partition coefficient, L/kg,
- $K_{ow}$  = octanol/water partition coefficient, dimensionless.

The partition coefficient obtained from Equation 49 provides the solid phase contaminant concentration on a volatile solids basis for primary solids, activated sludge and digested sludge.

Sorption and desorption of contaminants by wastewater treatment plant solids has been observed to be a relatively rapid process. *TOXCHEM+* therefore assumes, that, as far as sorption is concerned, the system is always in equilibrium. In other words, it is assumed that sorption equilibrium is attained instantaneously in all parts of the system.

Contaminants can also sorb into oils which may be present in the wastewater. Sorption of contaminants into oil is handled similarly to sorption onto solids. It is also assumed that sorption and desorption by oil is a rapid process and that the system is always in equilibrium with respect to sorption into oil.

Partitioning of contaminants between oil and water has been represented by the octanol/water partition coefficient (Barbari and King, 1982). Therefore, in an oil/water system, at equilibrium, the concentration of a contaminant in the oil can be expressed by:

$$C_{oil} = K_{ow} C \quad (50)$$

where,

$C_{oil}$  = concentration of contaminant in oil phase, mg/kg.

The portion of the total concentration of a contaminant which is sorbed onto solids is:

$$C_{ss} = K_p X C \quad (51)$$

where,

$C_{ss}$  = concentration of contaminant in wastewater sorbed on solids, mg/m<sup>3</sup>,  
 $X$  = volatile suspended solids (VSS) concentration, kg/m<sup>3</sup>.

The portion of the total concentration of a contaminant which is sorbed into oil is:

$$C_{so} = K_{ow} \frac{O}{d_o} C \quad (52)$$

where,

$C_{so}$  = concentration of contaminant in wastewater sorbed in oil, mg/m<sup>3</sup>,  
 $O$  = oil concentration in wastewater, kg/m<sup>3</sup>,  
 $d_o$  = density of oil, kg/m<sup>3</sup>.

The density of the oil is assumed to be 870 kg/m<sup>3</sup>.

The total concentration of a contaminant in wastewater is:

$$C_{tot} = (1 + K_p X + K_{ow} \frac{O}{d_o}) C = (1 + S) C \quad (53)$$

where,

$C_{tot}$  = total concentration of contaminant in wastewater, mg/m<sup>3</sup>,

and

$$S = K_p X + K_{ow} \frac{O}{d_o} \quad (54)$$

Where the separation of oil is not specified in a process, the oil concentration in the effluent and sludge streams are taken to be equal to the concentration in the influent stream. In suspended growth biological treatment processes the oil is assumed to be completely biodegraded. Contaminants sorbed to the oil are accounted for in the mass balance equations.

### 1.3 Biodegradation

#### 1.3.1 Suspended Growth Processes

A number of mathematical expressions have been used to describe the rate of biodegradation of organic compounds (e.g., the Monod equation). Toxic contaminants are generally present at low concentrations in wastewater treatment plants. At low substrate concentrations, it has been demonstrated that the biodegradation rate can be expressed as a mixed second order reaction. In fact, the Monod equation and other rate expressions can be approximated by a mixed second order rate expression at low substrate concentration. The form of the rate expression for low substrate concentration is:

$$r_b = k_b X C V \quad (55)$$

where,

- $r_b$  = biodegradation rate, mg/h,
- $k_b$  = biodegradation rate coefficient,  $\text{m}^3/\text{kg}\cdot\text{h}$ ,
- $X$  = biomass concentration,  $\text{kg}/\text{m}^3$ ,
- $C$  = contaminant concentration,  $\text{mg}/\text{m}^3$ .

**TOXCHEM+** uses Equation 55 to model biodegradation in all suspended growth biological treatment processes. The biomass concentration is taken to be the volatile suspended solids (VSS) concentration.

#### 1.3.2 Biofilm Processes

In processes such as trickling filters and rotating biological contactors (RBCs), the biomass is attached to surfaces as a biofilm. Usually, toxics in wastewater are present at trace concentrations in an aqueous media which contains higher concentrations of other organics that act as a primary substrate. It is assumed that biofilm thickness and density will be defined by the primary substrate and therefore, the biodegradation kinetics of the trace contaminants are assumed as:

$$r_b = k_b X_f C V \quad (56)$$

where,

- $r_b$  = rate of biodegradation,  $\text{mg}/\text{hr}$ ,
- $k_b$  = biodegradation rate coefficient,  $\text{m}^3/\text{kg}\cdot\text{h}$ ,
- $X_f$  = biofilm density,  $\text{kg}/\text{m}^3$ ,
- $C$  = contaminant concentration,  $\text{mg}/\text{m}^3$ .

An effective diffusion layer is assumed to exist between the bulk liquid phase and the biomass surface. The following terms are defined:

- $C_b$  = contaminant concentration in bulk liquid layer,  $\text{mg}/\text{m}^3$ ,
- $C_s$  = contaminant concentration at outer edge of biofilm,  $\text{mg}/\text{m}^3$ ,
- $L_f$  = biofilm thickness,  $\text{m}$ ,
- $z$  = distance in biofilm as measured from liquid interface,  $\text{m}$ .

In **TOXCHEM+**,  $L_f$  is assigned a value of 0.1 mm.

The following boundary conditions are assumed for the biofilm:

$$\begin{aligned} C &= C_s \text{ at } z = 0 \\ dC/dz &= 0 \text{ at } z = L_f \end{aligned}$$

The governing equation for diffusion and biodegradation in the biofilm at steady state is:

$$D_e \frac{\partial^2 C}{\partial z^2} = k_b X_f C \quad (57)$$

where,

$D_e$  = contaminant diffusion coefficient in biofilm,  $m^2/h$ .

In the program,  $D_e$  is assigned a value of 80% of the contaminant's water phase diffusion coefficient.

Solving Equation 57 with the previously stated boundary conditions yields:

$$C = C_s \frac{\cosh[r_1 (L_f - z)]}{\cosh(r_1 L_f)} \quad (58)$$

where,

$$\cosh(u) = 0.5(e^u + e^{-u}) \quad (59)$$

and,

$$r_1 = \sqrt{\frac{X_f k_b}{D_e}} \quad (60)$$

The contaminant mass flux at the biofilm-stagnant layer boundary ( $z = 0$ ) is defined as:

$$N_s = D_e \frac{dC}{dz} \quad (61)$$

where,

$N_s$  = mass flux into biofilm,  $mg/m^2 \cdot h$ .

Differentiating Equation 58 and substituting into Equation 60 yields:

$$N_s = D_e r_1 \tanh(r_1 L_f) C_s \quad (62)$$

The flux through the stagnant layer (external resistance) must equal the flux into the biomass, and therefore:

$$D_e r_1 \tanh(r_1 L_f) C_s = k_L (C_b - C_s) \quad (63)$$

where,

$k_L$  = external mass transfer coefficient, m/hr.

The external mass transfer coefficient might be approximated by:

$$k_L = \frac{D_e}{L} \quad (64)$$

where,

$D_e$  = contaminant diffusion coefficient in water,  $m^2/h$ ,  
 $L$  = thickness of stagnant layer, m.

In *TOXCHEM+*,  $L$  is assigned a value of 0.1 mm.

Equation 63 can be solved for  $C_s$  and the resulting equation can be substituted into:

$$N_s = k_L (C_b - C_s) \quad (65)$$

to yield:

$$N_s = k_L \frac{D_e r_1 \tanh(r_1 L_f)}{D_e r_1 \tanh(r_1 L_f) + k_L} C_b \quad (66)$$

This equation relates the mass flux into the biofilm to the bulk phase concentration and does not require iterative solutions. When  $k_L$  is very large, it reduces to:

$$N_s = D_e r_1 \tanh(r_1 L_f) C_b \quad (67)$$

When  $k_L$  is very small it reduces to:

$$N_s = k_L C_b \quad (68)$$

## 1.4 Temperature Correction of Sensitive Parameters

Industrial and municipal wastewater treatment plants are subject to variations in wastewater temperature. The wastewater temperature can significantly influence the fate of trace contaminants in wastewater treatment plants. To account for temperature effects, *TOXCHEM+* incorporates temperature correction for the Henry's Law coefficient and the biodegradation rate coefficients.

### 1.4.1 Henry's Law Coefficient

The following relationship has been used to estimate Henry's Law coefficients at different temperatures:

$$H = \frac{\exp(A - \frac{B}{T})}{RT} \quad (69)$$

where,

- H = Henry's Law coefficient, m<sup>3</sup> liquid/m<sup>3</sup> gas,
- A = compound specific parameter, dimensionless,
- B = compound specific parameter, dimensionless,
- T = temperature, °K,
- R = gas constant = 8.2057 x 10<sup>-5</sup> atm • m<sup>3</sup>/mole • °K.

Unfortunately, the parameters A and B are not available for all compounds of interest. However, Henry's Law coefficients have been determined for a large number of compounds at 25 °C. If the Henry's Law coefficient is known at 25 °C, the following relationship can be used to estimate the coefficient at a different temperature:

$$H = H_{25} \Theta^{(T - 25)} \quad (70)$$

where,

- H = Henry's Law coefficient at T°C, m<sup>3</sup> liquid/m<sup>3</sup> gas,
- H<sub>25</sub> = Henry's Law coefficient at 25°C, m<sup>3</sup> liquid/m<sup>3</sup> gas,
- T = temperature, °C,
- Θ = temperature correction factor, dimensionless.

The data of Gossett (1987) was examined to evaluate the applicability of this relationship to a number of compounds. In the Gossett study, the influence of temperature on the Henry's Law coefficients of 13 compounds was evaluated. The modified van't Hoff relationship was linearly regressed with all of the Gossett data to estimate Θ. The results of this regression indicated a best fit value for Θ of 1.044 with 95% confidence limits of 0.0035. From the narrow confidence limits of the estimated Θ value it was apparent that Equation 70 can reasonably predict the temperature influence on Henry's Law coefficients and was therefore incorporated into **TOXCHEM+** as:

$$H = H_{25} 1.044^{(T - 25)} \quad (71)$$

**TOXCHEM+** uses Equation 69 to estimate the Henry's Law coefficient for compounds with available A and B parameters. For other compounds, Equation 70 is used to correct the data base value to temperatures other than 25°C.

#### 1.4.2 Biodegradation Rate Constants

The effect of temperature on biological processes is usually expressed in the form:

$$k_b = k_{b20} \Theta^{(T - 20)} \quad (72)$$



where,

- $k_b$  = biodegradation rate coefficient at  $T^\circ\text{C}$ ,  $\text{m}^3/\text{kg}\cdot\text{h}$ ,
- $k_{b20}$  = biodegradation rate coefficient at  $20^\circ\text{C}$ ,  $\text{m}^3/\text{kg}\cdot\text{h}$ ,
- $\Theta$  = temperature correction factor, dimensionless,
- $T$  = temperature,  $^\circ\text{C}$ .

A typical value reported for  $\Theta$  for activated sludge systems is 1.04 (Metcalf and Eddy, 1991). As there is little information on the influence of temperature on the biodegradation rate of trace organics, the following relationship is incorporated into *TOXCHEM+* to adjust the aerobic biodegradation rate coefficients:

$$k_b = k_{b20} 1.04^{(T - 20)} \quad (73)$$

For anaerobic biodegradation the same  $\Theta$  value is used as for aerobic biodegradation except that the rate coefficients in the database are entered at  $35^\circ\text{C}$ . Therefore, the following relationship is used for temperature correction of anaerobic biodegradation rate coefficients:

$$k_b = k_{b35} 1.04^{(T - 35)} \quad (74)$$

## 2. Unit Process Mass Balances

In the *TOXCHEM+* models, the fate of hazardous trace organics is simulated in a number of unit processes. Three removal mechanisms are considered: (1) volatilization (including air stripping and surface volatilization), (2) sorption onto solids, and (3) biodegradation. The mathematical basis for the toxic contaminant process simulation is based upon mass balances on the contaminant around each unit process. The mass balance equations for all of the processes in the treatment system are solved simultaneously by the *TOXCHEM+* program to determine the fate of the contaminants. The following sections provide details on the model formulations and assumptions.

### 2.1 Open Versus Covered Unit Processes

The following sections document the derivation of the models present in the *TOXCHEM+* software package. In all cases, the derivations are presented for cases in which the unit process is covered and vented. In these cases simultaneous solution of the gas and liquid phase mass balance equations is performed. For situations when the processes are open to the atmosphere, it is assumed that the gas phase contaminants are continuously swept away from the water surface. Therefore, the gas phase concentration is assumed to be zero, and only the liquid phase mass balance is solved.

For all covered processes, except flow through ventilated sewers, the wind speed is taken to be zero for estimating surface volatilization rate coefficients. For open processes the wind speed is set to the user specified value.

### 2.2 Sewer Reaches

Sewer reaches are modelled as a user-prescribed number of continuous-flow stirred tank reactors (CSTRs) in series in both the gaseous and liquid phases. Reactors in each phase are all of equal length. Depending on how the sewer reach is set up, two different air flow conditions can be modelled. If an air influent is connected to the sewer reach, the air flow will be modelled as a flow through system

(i.e., flowing through each gas phase CSTR in series). The air influent to the sewer reach may come from the air influent process and/or from the air effluent of any other process. If no air influent is connected to the sewer reach, uniform ventilation will be assumed. In that case the total air flow rate is specified by the user as a fraction of the water flow rate. With uniform ventilation the total air flow rate is divided equally to each gas phase CSTR. Each gas phase CSTR is separately ventilated and not connected to the other gas phase CSTRs. Uncontaminated air is assumed to enter each CSTR from the atmosphere at the appropriate flow rate and is discharged separately from each CSTR. For the uniform ventilation case, the air effluent from a sewer reach is the sum of the effluents from each CSTR.

The steady state mass balance equations for contaminant transport in each CSTR are:

*Liquid Phase:*

$$Q (1 + S_o) (C_{i-1} - C_i) - K_L (C_i - \frac{C_{gi}}{H}) A_i = 0 \quad (75)$$

*Gas Phase:*

$$Q_g (C_g^* - C_{gi}) + K_L (C_i - \frac{C_{gi}}{H}) A_i = 0 \quad (76)$$

where,

- $C_i$  = contaminant concentration in liquid CSTR i, mg/m<sup>3</sup>,
- $C_{i-1}$  = contaminant concentration in liquid CSTR i-1, i.e., CSTR immediately upstream of i, mg/m<sup>3</sup>,
- $C_{gi}$  = contaminant concentration in gaseous CSTR i, mg/m<sup>3</sup>,
- $C_g^*$  = ambient contaminant concentration if uniform ventilation, or  $C_{g,i-1}$  if flow-through type ventilation, mg/m<sup>3</sup>,
- $C_{g,i-1}$  = contaminant concentration in gaseous CSTR i-1, i.e., CSTR immediately upstream of i, mg/m<sup>3</sup>,
- $S_o$  = influent sorption term, dimensionless (see Section 1.2),
- $Q$  = wastewater flow rate, m<sup>3</sup>/h,
- $Q_g$  = headspace ventilation rate, m<sup>3</sup>/h,
- $K_L$  = overall mass transfer coefficient, m/h,
- $H$  = Henry's Law coefficient, m<sup>3</sup> liquid/m<sup>3</sup> gas,
- $A_i$  = interfacial surface area for each CSTR, m<sup>2</sup>.

Wastewater flow rate (Q) and headspace ventilation rate (Q<sub>g</sub>) (air flow rate) are prescribed by the user. Wastewater flow rate is used in conjunction with Manning's equation and user-prescribed reach characteristics (channel slope, diameter, roughness coefficient) to solve for depth of water flow. This in turn is used to calculate interfacial surface area (A<sub>i</sub>) for each CSTR. The total headspace ventilation rate is either entered as a user-prescribed fraction of the liquid flow rate or is calculated from the specified air influent streams. For uniform ventilation the total headspace ventilation rate is divided equally between the gas phase CSTRs.

The overall mass transfer coefficient ( $K_L$ ) is estimated as described in Section 1.1.4.

## 2.3 Drops

Assuming that the headspace in the drop structure is well-mixed, a gas-phase mass balance leads to:

$$Q_g (C_{g0} - C_g) + Q (1 + S_o) (C_o - C) = 0 \quad (77)$$

where,

- $Q_g$  = gas flow rate through drop structure,  $m^3/h$ ,
- $C_{g0}$  = contaminant concentration in air influent,  $mg/m^3$ ,
- $C_g$  = contaminant concentration in air effluent,  $mg/m^3$ ,
- $Q$  = wastewater flow rate,  $m^3/h$ ,
- $C_o$  = wastewater influent contaminant concentration,  $mg/m^3$ ,
- $C$  = wastewater effluent contaminant concentration,  $mg/m^3$ .

Equation 77 is solved simultaneously with Equation 46 (Section 1.1.5) to determine the gas and liquid effluent concentrations.

## 2.4 Grit Chambers

The grit chamber is assumed to be a completely mixed continuous flow stirred tank reactor (CSTR). Volatilization and stripping to bubbles, when applicable, are assumed to be the only removal mechanisms. The mass balance equations for the grit chamber are:

*Liquid Phase:*

$$Q (1 + S_o) (C_o - C) - V [k_v (C - \frac{C_g}{H}) + k_s C] = 0 \quad (78)$$

*Gas Phase:*

$$V [k_v (C - \frac{C_g}{H}) + k_s C] - Q_g C_g = 0 \quad (79)$$

where,

- $Q$  = wastewater flow rate,  $m^3/h$ ,
- $C_o$  = influent contaminant concentration,  $mg/m^3$ ,
- $C$  = effluent contaminant concentration,  $mg/m^3$ ,
- $C_g$  = gas phase contaminant concentration,  $mg/m^3$ ,
- $H$  = Henry's Law coefficient,  $m^3 \text{ liquid}/m^3 \text{ gas}$ ,
- $V$  = volume of process vessel,  $m^3$ ,
- $k_v$  = surface volatilization rate constant,  $h^{-1}$ ,
- $k_s$  = air stripping rate constant,  $h^{-1}$ .

The surface volatilization rate constant is estimated as described in Section 1.1.1. For aerated grit chambers, the air stripping rate constant is estimated as described in Section 1.1.2 under *Diffused Bubble Aeration*. For grit chambers the oxygen transfer efficiency is generally not known. An oxygen transfer efficiency of 2% is assumed for the grit chamber.

## 2.5 Clarifiers

The bulk volume of the clarifier is modelled as a CSTR. The liquid phase contaminant concentration in the sludge waste stream is assumed to be equal to the clarifier influent liquid phase contaminant concentration. Contaminants entering the clarifier can undergo liquid-gas mass transfer from the quiescent surface and from the weirs.

The mass balance equations for the clarifier are:

*Liquid Phase:*

$$Q(1 + S_o)C_o - Q_w(1 + S_w)C_o - Q_e(1 + S_e)C - V k_v \left(C - \frac{C_g}{H}\right) = 0 \quad (80)$$

*Gas Phase:*

$$V k_v \left(C - \frac{C_g}{H}\right) + Q_e(1 + S_e)(C - C_e) - Q_g C_g = 0 \quad (81)$$

where,

- $Q_w$  = wasting flow rate, m<sup>3</sup>/h,
- $Q_e$  = effluent flow rate, m<sup>3</sup>/h, =  $Q - Q_w$ ,
- $C_o$  = contaminant concentration in clarifier influent, mg/m<sup>3</sup>,
- $C$  = contaminant concentration in clarifier prior to weir, mg/m<sup>3</sup>,
- $C_e$  = contaminant concentration in clarifier effluent after weir, mg/m<sup>3</sup>,
- $S_w$  = waste sludge sorption term, dimensionless (see Section 1.2),
- $S_e$  = effluent sorption term, dimensionless (see Section 1.2).

The concentration change across the weir is determined by applying Equation 38 (Section 1.1.1):

$$\left(C - \frac{C_g}{H}\right) \exp \left[ -A \frac{D_c}{D_{oxy}} \left( \frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} - C_e = 0 \quad (82)$$

The surface volatilization rate constant is estimated as described in Section 1.1.1.

The concentrations of the contaminant in the clarifier contents, the clarifier effluent and the vent gas are determined by solving Equations 80, 81 and 82.

## 2.6 Equalization Basins

Equalization basins are modelled as completely mixed reactors with surface volatilization as the only removal mechanism. The mass balance equations for an equalization basin are:

*Liquid Phase:*

$$Q (1 + S_o) (C_o - C) - V k_v (C - \frac{C_g}{H}) = 0 \quad (83)$$

*Gas Phase:*

$$V k_v (C - \frac{C_g}{H}) - Q_g C_g = 0 \quad (84)$$

The surface volatilization rate constant is estimated as described in Section 1.1.1.

## 2.7 Channels

Channels are modelled as ten CSTRs in series in the liquid and gas phases. The channel can be either diffused bubble aerated or non-aerated. The removal mechanisms are surface volatilization and stripping by diffused bubble aeration when applicable. The program solves a mass balance equation for each CSTR. The mass balance equations for the *i*th CSTR are:

*Liquid Phase:*

$$Q (1 + S_o) (C_{i-1} - C_i) - \frac{V}{10} [k_v (C_i - \frac{C_{gi}}{H}) + k_s C_i] = 0 \quad (85)$$

*Gas phase:*

$$\frac{V}{10} [k_v (C_i - \frac{C_{gi}}{H}) + k_s C_i] - Q_g C_{gi} = 0 \quad (86)$$

where,

- $C_{i-1}$  = contaminant concentration in influent of *i*th CSTR, mg/m<sup>3</sup>,
- $C_i$  = contaminant concentration in effluent of *i*th CSTR, mg/m<sup>3</sup>,
- $C_g$  = contaminant concentration in gas phase of *i*th CSTR, mg/m<sup>3</sup>.

The surface volatilization rate constant is estimated as described in Section 1.1.1. For aerated channels, the air stripping rate constant is estimated as described in Section 1.1.2 under Diffused Bubble Aeration. For channels, the oxygen transfer efficiency is generally not known. An oxygen transfer efficiency of 2% is assumed for the channels.

## 2.8 Dissolved Air Flotation

Dissolved air flotation (DAF) is commonly employed to either separate oils from wastewater streams or for thickening of waste activated sludges. The dissolved air flotation model can simulate either of these scenarios. The partitioning of contaminants between oil and aqueous phases is assumed to be represented by the compounds octanol-water partition coefficient (Barbari and King, 1982). Contaminants entering and leaving the flotation basin in the liquid phase are assumed to be partitioned in equilibrium between the water and oil phases. Contaminants leaving the basin in the float are assumed to be partitioned in

equilibrium with the water phase contaminant concentration in the tank prior to the weir. Surface volatilization is assumed to be equivalent to that observed in aqueous systems. Gas phase concentrations of the contaminants in the air evolved in the flotation basin are assumed to be in equilibrium with respect to the liquid phase concentration in the tank and the compound's Henry's Law coefficient.

It is assumed that the water leaving the DAF passes over a weir. The volatilization from the weir is estimated in the same manner as for a primary clarifier.

The mass balance equations for the dissolved air flotation process are:

*Liquid Phase:*

$$Q(1 + S_o)C_o - Q_w(1 + S_w)C - Q_e(1 + S_e)C - Q_aHC - V k_v \left(C - \frac{C_g}{H}\right) = 0 \quad (87)$$

*Gas Phase:*

$$V k_v \left(C - \frac{C_g}{H}\right) + Q_aHC + Q_e(1 + S_e)(C - C_e) - Q_gC_g = 0 \quad (88)$$

where,

- $Q_w$  = float wasting flow rate, m<sup>3</sup>/h,
- $Q_e$  = effluent flow rate, m<sup>3</sup>/h =  $Q_o - Q_w$ ,
- $Q_a$  = flotation air flow rate, m<sup>3</sup>/h,
- $C_o$  = contaminant concentration in influent, mg/m<sup>3</sup>,
- $C$  = contaminant concentration in tank prior to weir, mg/m<sup>3</sup>,
- $C_e$  = contaminant concentration in effluent after weir, mg/m<sup>3</sup>.

The concentration change across the weir is determined by applying Equation 38 (Section 1.1.1):

$$\left(C - \frac{C_g}{H}\right) \exp \left[ -A \frac{D_c}{D_{oxy}} \left( \frac{100H}{100H + 1} \right) \right] + \frac{C_g}{H} - C_e = 0 \quad (89)$$

The surface volatilization rate constant is estimated as described in Section 1.1.1.

The concentrations of the contaminant in the DAF contents, the DAF effluent and the vent gas are determined by solving Equations 87, 88 and 89 simultaneously.

## 2.9 Diffused Bubble Aeration Basins

Diffused bubble aeration basins are modelled as a user-specified number of CSTRs in series in both the liquid and gas phases. Surface volatilization, stripping to air bubbles, and biodegradation are assumed to be the only removal mechanisms. The mass balance equations for the *i*th CSTR in the diffused bubble aeration basin are:

*Liquid Phase:*

$$Q [(1 + S_o) C_{i-1} - (1 + S_m) C_i] - \frac{V}{N} [k_v (C_i - \frac{C_{gi}}{H}) + (k_s + k_b X_m) C_i] = 0 \quad (90)$$

*Gas Phase:*

$$\frac{V}{N} [k_v (C_i - \frac{C_{gi}}{H}) + k_s C_i] - Q_g C_{gi} = 0 \quad (91)$$

where,

- $S_m$  = mixed liquor sorption term, dimensionless (see Section 1.2),
- $N$  = number of CSTRs in series, dimensionless,
- $k_b$  = biodegradation rate constant,  $m^3/kg \cdot h$ .

The vent flow rate ( $Q_g$ ) must be greater than or equal to the aeration flow rate through the diffusers. If a lower vent flow rate is specified, the program will set the vent flow rate equal to the aeration flow rate.

The surface volatilization rate constant is estimated as described in Section 1.1.1. The air stripping rate constant is estimated as described in Section 1.1.2 under Diffused Bubble Aeration. The biodegradation rate constant is obtained from the compound data base.

The  $N$  liquid phase mass balance equations are solved simultaneously with the  $N$  gas phase equations.

## 2.10 Mechanical Aeration Basins

Aeration basins employing mechanical aerators are modelled as a user specified number of CSTRs in series in both the liquid and gas phases. Surface volatilization, air stripping, and biodegradation are assumed to be the only removal mechanisms. The mass balance equations for the  $i$ th CSTR in a mechanical aeration basin are:

*Liquid Phase:*

$$Q [(1 + S_o) C_{i-1} - (1 + S_m) C_i] - \frac{V}{N} [(k_v + k_s) (C_i - \frac{C_{gi}}{H}) + k_b X_m C_i] = 0 \quad (92)$$

*Gas Phase:*

$$\frac{V}{N} (k_v + k_s) (C_i - \frac{C_{gi}}{H}) - Q_g C_{gi} = 0 \quad (93)$$

The surface volatilization rate constant is estimated as described in Section 1.1.1. The air stripping rate constant is estimated as described in Section 1.1.2 under *Mechanical Aeration*. The biodegradation rate constant is obtained from the compound data base.

The  $N$  liquid phase mass balance equations are solved simultaneously with the  $N$  gas phase equations.

## 2.11 Combined Diffused and Mechanical Aeration Basins

Aeration basins employing both diffused and mechanical aeration are modelled as a user specified number of CSTRs in series in both the liquid and gas phases. Surface volatilization, air stripping, and biodegradation are assumed to be the only removal mechanisms. The model for aeration basins that employ both mechanical and diffused aeration has stripping rate coefficients associated with each of these aeration mechanisms. Therefore, the mass balance equations for the  $i$ th CSTR are:

*Liquid Phase:*

$$Q[(1 + S_o)C_{i-1} - (1 + S_m)C_i] - \frac{V}{N}[(k_{sm} + k_v)(C_i - \frac{C_{gi}}{H}) + (k_{sd} + k_b X_m)C_i] = 0 \quad (94)$$

*Gas Phase:*

$$\frac{V}{N}[(k_v + k_{sm})(C_i - \frac{C_{gi}}{H}) + k_{sd}C_i] - Q_g C_{gi} = 0 \quad (95)$$

where,

$k_{sm}$  = stripping rate constant for mechanical aeration,  $h^{-1}$ ,

$k_{sd}$  = stripping rate constant for diffused aeration,  $h^{-1}$ .

The vent flow rate ( $Q_g$ ) must be greater than or equal to the aeration flow rate through the diffusers. If a lower vent flow rate is specified, the program will set the vent flow rate equal to the aeration flow rate.

The surface volatilization rate constant is estimated as described in Section 1.1.1. The air stripping rate constants are estimated as described in Section 1.1.2. The biodegradation rate constant is obtained from the compound data base.

The  $N$  liquid phase mass balance equations are solved simultaneously with the  $N$  gas phase equations.

## 2.12 Trickling Filters

Trickling filters consist of a packed bed which has a biofilm layer growing on it. Various packings such as gravel, Raschig rings, etc. have been employed. However, at present most trickling filters are constructed of modular sheet packing. Wastewater is spread over the surface of the bed and allowed to trickle down over the biofilm. Contaminants in the wastewater diffuse into the biofilm where they are biodegraded. Excess biomass will slough off and be carried away by the wastewater stream. Oxygen supply to the process is generally provided by natural advection which is created by temperature differences between the surrounding air and the wastewater stream. In some cases air is supplied by forced ventilation.

Volatile contaminants may be transferred from wastewater to air as the wastewater trickles over the packing material. The airborne contaminants are then carried out of the reactor by the same movement of gas which is responsible for oxygen supply.



The model for the trickling filter process employs the following assumptions:

- steady state with respect to time,
- the wastewater flows down the media in a plug flow regime,
- the air stream flows counter-current to the liquid stream in a plug flow regime,
- the background gas phase concentrations of the contaminants are negligible,
- the biofilm is modelled as follows:
  - there is an stagnant liquid layer between the bulk liquid and the biofilm and this provides an external mass transfer resistance,
  - the rate of biodegradation is first order with respect to biomass concentration and contaminant concentration,
  - there is an internal diffusional resistance through the biofilm,
  - the biofilm is of constant thickness and density for the entire process.

The liquid phase and gas phase mass balance equations for a horizontal differential slice of the reactor are:

*Liquid Phase:*

$$QdC = -(N_v + N_b) aA_x dz \quad (96)$$

*Gas Phase:*

$$Q_g dC_g = -N_v aA_x dz \quad (97)$$

where,

- $N_v$  = mass flux out of slice due to volatilization,  $\text{mg}/\text{m}^2 \cdot \text{h}$ ,
- $N_b$  = mass flux out of slice due to biodegradation,  $\text{mg}/\text{m}^2 \cdot \text{h}$ ,
- $a$  = specific interfacial area of trickling filter media,  $\text{m}^2/\text{m}^3$ ,
- $A_x$  = cross-sectional area of the trickling filter,  $\text{m}^2$ ,
- $z$  = depth of the trickling filter,  $\text{m}$ .

The mass transfer flux due to volatilization is:

$$N_v = K_v \left( C - \frac{C_g}{H} \right) \quad (98)$$

where,

$K_v$  = volatilization mass transfer coefficient,  $\text{m}/\text{h}$ .

The mass transfer flux due to biodegradation is defined as (see Section 1.3.2):

$$N_b = k_L \frac{D_e r_1 \tanh(r_1 L_f)}{D_e r_1 \tanh(r_1 L_f) + k_L} C \quad (99)$$

where,

$$r_1 = \sqrt{\frac{X_f k_b}{D_e}} \quad (100)$$

and,

- $k_L$  = stagnant layer mass transfer coefficient, m/h,
- $X_f$  = biomass density, kg/m<sup>3</sup>,
- $k_b$  = biodegradation rate constant, m<sup>3</sup>/kg•h,
- $D_e$  = Diffusion coefficient in biofilm layer, m<sup>2</sup>/h,
- $L_f$  = biofilm thickness, m.

A default value for the oxygen mass transfer coefficient of 0.2 m/d is included in the trickling filter process input parameters. The value is based on pilot plant trickling filter experiments. A different value may be specified by the user. The volatilization mass transfer coefficient is calculated from the oxygen mass transfer coefficient using Equations 20 and 23 (Section 1.1.2). For the trickling filter a  $k_G/k_L$  ratio of 4 is used.

The biodegradation rate coefficient is obtained from the compound data base and is the same as the coefficient used for aerobic suspended growth processes. Contaminants sorbed onto solids or oil in the influent are assumed to not be available for volatilization or biodegradation in the trickling filter.

Equations 96 and 97 are solved simultaneously to predict the concentrations of contaminants through the depth of the filter in each phase.

## 2.13 Rotating Biological Contactors

Rotating biological contactors (RBCs) consist of biofilm covered discs rotating in a basin through which a wastewater stream flows. The discs are only partially submerged in the wastewater, and hence, wastewater is picked up as the revolving disc leaves the water and is carried around by the rotation of the disc. This allows a transfer of oxygen into the wastewater to occur on the non-submerged portion of the disc. A majority of the organic contaminant removal is expected to result from diffusion of the contaminants into the biofilm, followed by subsequent biodegradation. Biodegradation of contaminants by suspended biomass in the basin is assumed to be negligible.

The RBC process is typically separated into a series of cells by baffles which segregate the wastewater basin. The headspace of the process can be either open to the atmosphere or covered. Forced ventilation of the headspace is not commonly employed.

In the RBC model, volatilization from the surface of the wastewater in the basin is assumed to be negligible with emissions dominated by volatilization from the film of wastewater that covers the rotating discs while not submerged in the wastewater basin.

The model for the RBC process employs the following assumptions:

- steady state with respect to time,
- each section of the wastewater basin is a CSTR,
- the headspace of the entire RBC is connected and considered as one CSTR,
- the background gas phase concentrations of the contaminants are negligible,
- the biofilm is modelled as follows:
  - there is a stagnant liquid layer between the bulk liquid and the biofilm and this provides an external mass transfer resistance,
  - the rate of biodegradation is first order with respect to biomass concentration and contaminant concentration,
  - there is an internal diffusional resistance through the biofilm,
  - the biofilm is of constant thickness and density for the entire process.

The mass balance equation for the liquid phase of the  $i$ th basin is:

$$Q (C_{i-1} - C_i) - N_{vi}A_{ei} - N_{bi}A_{ti} = 0 \quad (101)$$

where,

- $N_{vi}$  = mass flux due to volatilization from  $i$ th CSTR,  $\text{mg}/\text{m}^2\cdot\text{h}$ ,
- $N_{bi}$  = mass flux due to biodegradation in  $i$ th CSTR,  $\text{mg}/\text{m}^2\cdot\text{h}$ ,
- $A_{ei}$  = exposed surface area of disks in  $i$ th CSTR,  $\text{m}^2$ ,
- $A_{ti}$  = total surface area of disks in  $i$ th CSTR,  $\text{m}^2$ .

The mass flux due to volatilization from each basin is described as:

$$N_{vi} = K_v (C_i - \frac{C_g}{H}) \quad (102)$$

where,

- $K_v$  = surface volatilization mass transfer coefficient,  $\text{m}/\text{h}$ .

The relationship defining mass flux due to biodegradation is the same as for a trickling filter (Equation 99). The surface area over which this mass flux occurs is assumed to be the total area of the discs which is present in the RBC section.

The mass balance on the RBC headspace is therefore:

$$\sum_{i=1}^N N_{vi} - Q_g C_g = 0 \quad (103)$$

where,

- $N$  = number of CSTRs, dimensionless.

A default value for the oxygen mass transfer coefficient of  $0.2 \text{ m}/\text{d}$  is included in the RBC process input parameters. The value is based on pilot plant RBC experiments. A different value may be specified by the user. The volatilization mass transfer coefficient is calculated from the oxygen mass transfer

coefficient using Equations 20 and 23 (Section 1.1.2). For the RBC a  $k_G/k_L$  ratio of 4 is used.

The biodegradation rate coefficient is obtained from the compound data base and is the same as the coefficient used for aerobic suspended growth processes.

The N liquid phase mass balance equations are solved simultaneously with Equation 103 to determine the liquid and gas phase concentrations of contaminants in the RBC.

## 2.14 Cooling Towers

Cooling towers are occasionally employed to cool wastewater prior to biological treatment. Contaminants may be transferred from wastewater to air as the wastewater trickles over the packing material. The contaminants are then carried out of the reactor by the same movement of gas which is responsible for wastewater cooling.

The model for the cooling tower process employs the following assumptions:

- steady state with respect to time,
- the wastewater flows down the media in a plug flow regime,
- the air stream flows counter-current to the liquid stream in a plug flow regime,
- the background gas phase concentrations of the contaminants are negligible.

Cooling towers are modelled similarly to trickling filters except that it is assumed that no biodegradation takes place. Therefore, the liquid phase and gas phase mass balance equations for a horizontal differential slice of the reactor are:

*Liquid Phase:*

$$Q dC = -N_v a A_x dz \quad (104)$$

*Gas phase:*

$$Q_g dC_g = -N_v a A_x dz \quad (105)$$

where,

- $N_v$  = mass flux out of slice due to volatilization,  $\text{mg}/\text{m}^2 \cdot \text{h}$ ,  
 $a$  = specific interfacial area of cooling tower media,  $\text{m}^2/\text{m}^3$ ,  
 $A_x$  = cross-sectional area of the cooling tower,  $\text{m}^2$ ,  
 $z$  = depth of the cooling tower,  $\text{m}$ .

The mass transfer flux due to volatilization is defined as:

$$N_v = K_v \left( C - \frac{C_g}{H} \right) \quad (106)$$

where,

- $K_v$  = volatilization mass transfer coefficient,  $\text{m}/\text{h}$ .

A value for the liquid film mass transfer coefficient of 0.8 m/d is used in the cooling tower process. The volatilization mass transfer coefficient is calculated from the oxygen mass transfer coefficient using Equations 20 and 23 (Section 1.1.2). For the cooling tower a  $k_G/k_L$  ratio of 700 is used.

Contaminants sorbed onto solids or oil in the influent are assumed to not be available for volatilization in the cooling tower.

Equations 104 and 105 are solved simultaneously to predict the concentrations of contaminants through the depth of the tower in each phase.

## 2.15 Polishing Ponds

Polishing ponds are modeled as completely mixed reactors with surface volatilization as the only removal mechanism. The effluent suspended solids from the pond is specified by the user. Solids removed (settled) in the pond are assumed to be degraded. The contaminants associated with the solids are thus available for volatilization or discharge in the effluent. The mass balance equations for an equalization basin are:

*Liquid Phase:*

$$Q [(1 + S_o) C_o - (1 + S_e) C] - V k_v (C - \frac{C_g}{H}) = 0 \quad (107)$$

*Gas Phase:*

$$V k_v (C - \frac{C_g}{H}) - Q_g C_g = 0 \quad (108)$$

The surface volatilization rate constant is estimated as described in Section 1.1.1.

## 2.16 Anaerobic Digestion

Anaerobic digesters are assumed to be completely mixed reactors with volatilization and biodegradation as the removal mechanisms. The biomass concentration in the digester is calculated as the influent volatile suspended solids (VSS) concentration minus the VSS reduction observed in the reactor. The model assumes that the offgas from the digestion process is in equilibrium with the digester liquid concentration and Henry's Law. The offgas flow is computed from the VSS reduction at a rate of 1.0 m<sup>3</sup> of offgas per kg of VSS removed. The mass balance equation for the anaerobic digester is:

$$Q [(1 + S_d) C_o - (1 + S_e) C] - V k_b X_d C - Q_g H C = 0 \quad (109)$$

where,

$S_d$  = sorption term in digester, dimensionless (see Section 1.2).

The biodegradation rate constant is obtained from the compound data base.

## 2.17 Aerobic Digestion

The aerobic digester is modelled as a user-specified number of completely mixed reactors in series in both the liquid and gas phases. The digester may have mechanical and/or diffused bubble aeration. The biomass concentration in the digester is calculated as the influent volatile suspended solids (VSS) concentration minus the VSS reduction observed in the reactor. Contaminants are assumed to be removed by surface volatilization, air stripping and biodegradation. The mass balance equations for the *i*th CSTR are:

*Liquid Phase:*

$$Q[(1 + S_o)C_{i-1} - (1 + S_d)C_i] - \frac{V}{N}[(k_{sm} + k_v)(C_i - \frac{C_{gi}}{H}) + (k_{sd} + k_b X_d)C_i] = 0 \quad (110)$$

*Gas Phase:*

$$\frac{V}{N}[(k_v + k_{sm})(C_i - \frac{C_{gi}}{H}) + k_{sd}C_i] - Q_g C_{gi} = 0 \quad (111)$$

where,

$k_{sm}$  = stripping rate constant for mechanical aeration,  $h^{-1}$ ,  
 $k_{sd}$  = stripping rate constant for diffused aeration,  $h^{-1}$ .

The vent flow rate ( $Q_g$ ) must be greater than or equal to the aeration flow rate through the diffusers. If a lower vent flow rate is specified, the program will set the vent flow rate equal to the aeration flow rate.

The surface volatilization rate constant is estimated as described in Section 1.1.1. The air stripping rate constants are estimated as described in Section 1.1.2. The biodegradation rate constant is obtained from the compound data base.

Equations 110 and 111 are solved simultaneously for the liquid and gas phase concentrations.

## 2.18 Sludge Dewatering

The sludge dewatering process is assumed to be a solids separation process without any volatilization, stripping or biodegradation. The mass balance equation for sludge dewatering is as follows:

$$[Q(1 + S_o) - Q_f(1 + S_f) - Q_s(1 + S_s)]C_o = 0 \quad (112)$$

where,

$Q_f$  = flow rate of filtrate or supernatant,  $m^3/h$ ,  
 $S_f$  = sorption term for filtrate or supernatant, dimensionless (see Section 1.2),  
 $Q_s$  = flow rate of dewatered sludge,  $m^3/h$ ,  
 $S_s$  = sorption term for dewatered sludge, dimensionless (see Section 1.2).

### 2.19 Centrifuge

The centrifuge is used for sludge dewatering. This process accounts for loss of contaminants due to volatilization from the sludge. An emission factor is computed for each compound as a function of the Henry's Law coefficient for the compound. The relationship between the Henry's Law coefficient and the emission factor was fitted from the PEEP study (Montgomery, 1990). The emission factors for the centrifuge are computed from the following relationship:

$$E = 1 - \exp(-0.577H) \quad (113)$$

where,

$E$  = fraction of contaminant emitted from process, dimensionless.

The rate of volatilization from the centrifuge is given by:

$$r_v = EQ (1 + S_o) C_o \quad (114)$$

where,

$r_v$  = rate of volatilization, mg/h.

### 2.20 Belt Filter Press

The belt filter press is used for sludge dewatering. This process accounts for loss of contaminants due to volatilization from the sludge. An emission factor is computed for each compound as a function of the Henry's Law coefficient for the compound. The relationship between the Henry's Law coefficient and the emission factor was fitted from the PEEP study (Montgomery, 1990). The emission factors for the belt filter press are computed from the following relationship:

$$E = 1 - \exp(-1.22H) \quad (115)$$

The rate of volatilization from the belt filter press is given by:

$$r_v = EQ (1 + S_o) C_o \quad (116)$$

### 2.21 Sludge Drying Bed

The sludge drying bed is used for sludge dewatering. This process accounts for loss of contaminants due to volatilization from the sludge. An emission factor is computed for each compound as a function of the Henry's Law coefficient for the compound. The relationship between the Henry's Law coefficient and the emission factor was fitted from the PEEP study (Montgomery, 1990). The emission factors for the sludge drying bed are computed from the following relationship:

$$E = 1 - \exp(-1.07H) \quad (117)$$

The rate of volatilization from the sludge drying bed is given by:

$$r_v = EQ (1 + S_o) C_o$$

(118)



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## 8. CONCLUSIONS AND RECOMMENDATIONS

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### 8.1 SUMMARY

In 1990, the Ontario Ministry of Environment and Energy (MOEE) listed as one of its areas of research needs "Volatile Chemicals in Sewers and their Treatment" (issue WA03). In July, 1991, the MOEE awarded a three-year grant to researchers at the University of Guelph to address the fundamental mechanisms which affect the fate of volatile organic compounds (VOCs) in wastewater collection systems. Combined with smaller amounts of NSERC and Environment Canada funding, funding from MOEE allowed the initiation of an intensive research program to study and improve the existing knowledge base related to the fate of volatile chemicals in sewers. Specific objectives included; (1) Assess the importance of competing fate mechanisms for VOCs in sewers, (2) Investigate gas-liquid mass transfer of VOCs along sewer reaches, (3) Quantify VOC emissions from a minimum of two municipal sewers in Toronto, and (4) Develop a model for predicting the fate of VOCs in wastewater collection systems.

A summary of major research components, important results and conclusions is provided in this report. Detailed descriptions of experimental methodologies and results are also provided in Volumes II through VIII. The collective results of this study shed a significant amount of new insight on the fate of VOCs in gravity-flow municipal sewers. They should facilitate future studies related to the fate of VOCs in both municipal and on-site industrial sewers. In particular, results should serve to illustrate the significant potential for VOC emissions from sewers. The experimental components of this research effort have lead to the development of a novel multi-reach VOC emissions model that should also be a valuable tool for future efforts to quantify emissions from sewers.

### 8.2 CONCLUSIONS

Descriptions of specific research components are provided in the preceding chapters of this report. In each case, specific conclusions are

provided. Rather than repeating all of those here, the three major conclusions which were drawn from this research effort are listed below.

1. Volatilization (gas-liquid mass transfer and ultimate discharge to the ambient atmosphere) is the major mechanism which affects the fate of VOCs in municipal sewers. Biodegradation should generally be considered negligible as a competing fate mechanism in sewers.
2. Significant quantities (on a relative or fractional basis) of VOCs may be emitted from municipal sewers to the ambient atmosphere prior to wastewater entering a treatment plant. This is particularly true for well-ventilated sewers consisting of numerous drop structures.
3. The fate of VOCs in municipal sewers may be estimated with a significant degree of accuracy given knowledge of several important system operating conditions, environmental variables, and chemical properties. At this time, the limiting factor associated with accurate fate estimation is the ability to routinely estimate natural ventilation of sewers.

It is clear, based on a review of published literature, that municipal wastewater collection systems have never been considered a major source of volatile or hazardous air pollutant emissions to the ambient atmosphere. The research effort described in this report does not prove otherwise, but does suggest that some sewers may emit significant quantities of potentially toxic and reactive VOCs. At the very least, the results of this study should provide motivation for continued study of municipal sewers as sources of VOC emissions in urban airsheds, and should also provide a framework upon which future research can be based. Several recommendations for future research are provided in Section 8.3.

### **8.3 RECOMMENDATIONS FOR FUTURE RESEARCH**

Although the results of this study significantly improve the existing knowledge-base associated with the fate of VOCs in sewers, it has also lead to

the realization of continued knowledge gaps. As such, the following recommendations are made for future research.

1. There is an obvious need for more research related to natural ventilation of municipal sewers. From a practical standpoint, it is recommended that a series of experiments be completed to quantify natural ventilation rates in a large number of operating sewers in Ontario. Such experiments could be completed by introducing an inert tracer such as sulfur hexafluoride into a sewer headspace, and collecting samples upstream and downstream of the tracer release over an extended period of time. This would allow determination of gas flow patterns, as well as gas flowrates, i.e., by tracer dilution. During each experiment, wastewater flow and fluid (temperature) conditions, as well as ambient and headspace gas conditions (temperature, pressure and wind speeds) should be monitored. It is recommended that ventilation rates be quantified in a minimum of eight operating sewers, twice each during summer and winter months. At a minimum, the results of these studies should provide some knowledge of "typical" ventilation rates.
2. Consistent with the first recommendation, it is recommended that fundamental research be completed to improve existing knowledge related to the mechanisms which induce natural ventilation of sewers. Without such research, it will not be possible to incorporate ventilation subroutines into existing sewer fate models. Research should be completed at the pilot scale, where mechanisms such as wastewater drag, thermal effects, wind effects, and wastewater displacement can be effectively controlled.
3. The sewer model described in Volume VIII should be applied to a major section of Toronto sewers, particularly in an area characterized by significant industrial discharges. Based on the results of this study, it may be appropriate to include the Massey Creek Interceptor in the model network. The modeling effort should consist of a model input phase during which time all required model inputs are collected. If possible, transient liquid flowrates should be quantified. Sewer ventilation rates

should also be estimated based on the use of gaseous tracer applications. This may be completed in conjunction with Recommendation 1 above.

4. The modeling effort described in Recommendation 3 should be coupled with extensive field monitoring to characterize average and transient VOC mass loadings (liquid phase) at various locations in the selected sewer system, including the headworks of the treatment plant which receives sewer effluent. If possible, sampling should be completed upstream and downstream of suspected major industrial dischargers. Samples should also be collected at various locations downstream of major dischargers. The results of field sampling can be used as model input, e.g., specific mass discharges to model nodes, as well as model evaluation, e.g., based on predicted and measured mass loadings downstream of major dischargers.
5. Results of field monitoring and model applications should be used to complete an assessment of the importance of VOC emissions from sewers. The assessment should include the impacts of hazardous air pollutant emissions on public health, as well as the contribution of sewers as sources of reactive organic gas emissions, i.e., precursors to ground-level ozone formation.
6. Based on the results of Recommendations 3 through 5, it may be necessary to consider methods for reducing or controlling VOC emissions from municipal sewers. In many cases, it may be possible to suppress emissions through relatively minor process modifications. It was beyond the scope of this study to complete an assessment of appropriate emission control technologies.

In addition to the research recommendations stated above, it is recommended that the sources of VOC discharges to the Massey Creek Interceptor be identified as soon as possible. Appropriate action should be taken to reduce such discharges. Source identification could be completed by upstream sampling to point of discharge using a portable GC with an appropriate detector, e.g., PID or MS. Portable purge and trap systems are now commercially-available for analysis of liquid samples in the field.



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